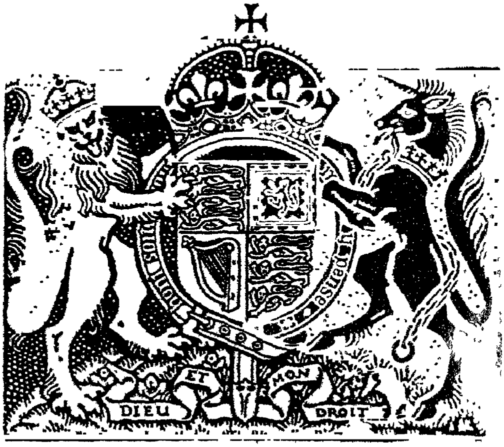

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INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

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1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3 \cdot [CH_2]_5 \cdot CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$ = propylmethane; $CH_3 \cdot CH(CH_3)_2$ = isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1} \cdot CH{:}CH \cdot C_nH_{2n+2}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus: $CH_3 \cdot CH{:}CH \cdot CH_3$ = α-dimethylethylene; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{:}C \cdot C_nH_{2n+1}$ and $C_nH_{2n+1} \cdot C{:}C \cdot C_nH_{2n+1}$. Adopt the same *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol: furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5 \cdot OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3 \cdot COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2{\cdot}COOH$, and not $C_6H_3(OC_2H_5)_2{\cdot}COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2{\cdot}NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

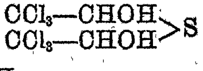
17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3{\cdot}CH(OEt)_2$ instead of

$$CCl_3{-}CH{<}\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}$$

$[CCl_3{\cdot}CH(OH)]_2S$ instead of

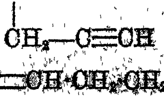


$$\begin{array}{l}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{array}{>}S$$

$CH_2 \vdots CH_2$ instead of $CH_2{=}CH_2$

$CH \vdots CH$ instead of $CH{\equiv}CH$

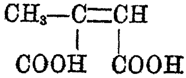
$CH \vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}C \vdots CH$ instead of



$$\begin{array}{l}CH_2{-}C{\equiv}CH\\|\\CH_2{-}C{\equiv}CH\end{array}$$

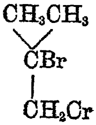
$CHMe \vdots CHPr^{\alpha}$ instead of $CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$

COOH·CH : CMe·COOH instead of



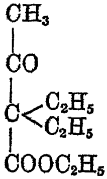
$$CH_3{-}\underset{COOH}{C}{=}\underset{COOH}{CH}$$

CH₂Br·CBrMe instead of

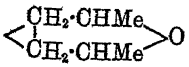


$$\begin{array}{l}CH_3CH_3\\ \quad\vee\\ \ CBr\\ \ \ |\\ CH_2Cr\end{array}$$

CEt₂Ac·COOEt instead of

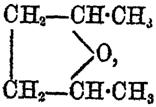


$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ C<^{C_2H_5}_{C_2H_5}\\ |\\ COOC_2H_5\end{array}$$



$$<^{CH_2·CHMe}_{CH_2·CHMe}>O$$

instead of

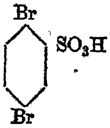


$$\begin{array}{l}CH_2—CH·CH_3\\ |\qquad\quad >O,\\ CH_2—CH·CH_3\end{array}$$

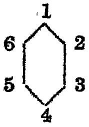
CHPh(OBz)·CH(OBz)·COOEt instead of
$C_6H_5·CH(O·CO·C_6H_5)·CH(O·COC_6H_5)·COOC_2H_5$.

19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2·SO_3H$[Br : SO_3H : Br = 1 : 2 : 4] instead of



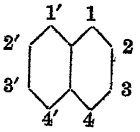
the figures always being used in the order



Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

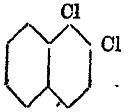
20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—

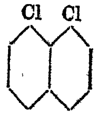


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—

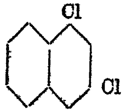
1 : 2 dichloro-
naphthalene =



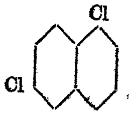
1 : 1′ dichloro-
naphthalene =



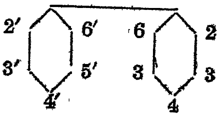
1 : 3 dichloro-
naphthalene =



1 : 3′ dichloro-
naphthalene =



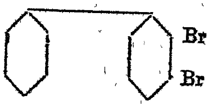
In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′. as shown by the following symbol:



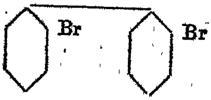
Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

and the two dibromodiphenyls

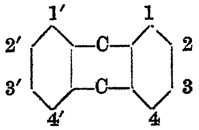


and



are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6].

In the case of anthracene, employ the following symbol, and indicate the position of the radicles relatively to the central C_2-group:



Examples:

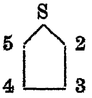
Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].
Purpurin, $C_6H_4 : C_2O_2 \cdot C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

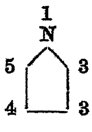
1 : 2 Dihydroxyanthraquinone = Alizarin.
1 : 4 „ = Quinizarin.
2 : 3′ „ = Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone = Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

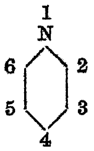
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

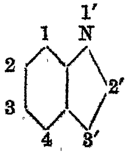


Pyrroline.

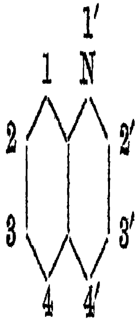


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Absorption-spectrum of Oxygen. By G. D. LIVEING and J. DEWAR (*Phil. Mag.* [5], 26, 286—290).—The absorption-spectrum of oxygen under pressure is examined by forcing it into a steel tube 165 cm. long, furnished with quartz windows at each end. At 85 atmos., bands were observed extending into the ultra-violet (λ 2664), beyond which the light appeared to be entirely absorbed. At 140 atmos., the bands were darker and the light ceased at λ 2704. A Rowland's grating failed to resolve the bands into lines, a result which agrees with Ångström's observation that the band a little above D in the solar spectrum is resolved into lines when the sun is high, but is continuous when the sun is near the horizon. On reducing the pressure, the band A was the last to disappear (at 20 atmos.). The bands appear to be identical with those of the solar spectrum which Ångström observed to be equally strong whether the atmosphere was moist or dry. Some of them are also identical with those observed by Olszewski with liquid oxygen. The point at which absorption of the ultra-violet begins is the same as that for ozone. Compounds of oxygen (carbonic anhydride and nitrous oxide) showed no absorption under pressure. In another experiment, a tube 18 m. long was used. At the ordinary pressure, the absorption of A was just visible. At 90 atmos., a general absorption in the red occurred extending to one-third the distance between A and B. The oxygen in this experiment was equal in quantity to that contained by a similar column extending to the limit of the atmosphere, but the absorption is much greater. Daylight, when observed through the tube, appeared to have a blue tint similar to that of liquid oxygen.

H. K. T.

Metallic Spectra. By J. TROWBRIDGE and W. C. SABINE (*Phil. Mag.* [5], 26, 342—353).—The authors have undertaken the re-examination of metallic spectra with a view to determine wave-lengths with greater accuracy. The apparatus used consisted of Rowland's grating with accessories arranged as previously described (*Phil. Mag.* [5], **16**, 197). Spectra of all orders are in focus at the same time, thus allowing a comparison of the different spectra and diminution of error. The photographic plate was also curved so that the distances between the lines were closely proportional. Solar and spark spectra were taken on different halves of the plate, the wave-lengths of the metallic lines being obtained by interpolation with the assistance of Rowland's tables of wave-lengths. In order to correct displacement due to vibration, the violet of the third spectrum was photographed along with the solar spectrum, and the wave-lengths obtained as before; the correction in some cases was as much as 20 millimetres. The noise of the spark discharge was found to be the cause of the vibration. A table of results is given. H. K. T.

Degree of Oxidation of Chromium and Manganese in Fluorescent Mixtures. By L. DE BOISBAUDRAN (*Compt. rend.*, **107**, 468—471).—Chromium oxide combines with aluminium oxide more readily the lower the temperature to which the latter has previously been heated. The colour of the product varies from rose to green as the quantity of chromium oxide added increases, the intermediate proportions yielding grey products. Presence of a trace of alkali somewhat facilitates combination, but the effect of the alkali varies with the relative proportions of the chromium and aluminium oxides and the alkali. When a precipitated mixture of chromium and aluminium oxides containing some alkali is heated, a small quantity of chromate is formed. If the quantity of chromium is very small, a large proportion of alkali prevents its union with the alumina.

Careful quantitative experiments failed to detect any loss of oxygen when the chromium and aluminium oxides are strongly heated, and hence there is no evidence that any chromous oxide is formed. The chromium in rubies is in all probability present in the state of chromic oxide. The rose-coloured compound seems to be the cause of the fluorescence, since the brilliancy of the latter increases with the intensity of the rose colour. C. H. B.

Electromotive Force of Amalgams. By S. LINDECK (*Ann. Phys. Chem.* [2], **35**, 311—331).—The author points out that experiments on the E.M.F. of amalgams containing varied proportions of mercury, immersed in an electrolyte such as sulphate of zinc or dilute sulphuric acid, have been made by Crova (*Ann. Chim. Phys.* [3], **69**, 458), Gaugain (*Compt. rend.*, **42**, 430), and Hockin and Taylor (*J. Soc. Tel. Eng.*, **8**, 282). The latter observers found that very minute traces of zinc or cadmium made a considerable difference in the E.M.F. of mercury. For example, an amalgam consisting of 1 part of zinc to 23·6 million parts of mercury in sulphate of zinc was found to be more positive than pure mercury by 0·01 volt, and an amalgam consisting of 1 part of cadmium in 5·7 million parts of mercury was found to be more positive by 0·09 volt than the pure metal.

The author has experimented with amalgams of zinc, cadmium, lead, tin, and silver, and constructed a series of curves in which the percentage of either of these metals contained in the mercury is taken as abscissa, and the corresponding change of potential difference as ordinate.

From the comparison of these curves he draws the following conclusions, which are in accordance with the results obtained by Taylor and Hockin:—

(1.) The higher the position of a metal in the electromotive series the more will the addition of a slight trace of it to pure mercury raise the position of the latter in the series.

(2.) A further addition of metal produces very little effect, and the amalgam containing a mere trace of the metal occupies approximately the same position in the series as a bar of amalgamated metal.

(3.) The amalgam of silver and mercury, in whatever proportions, occupies practically the same position in the series as that occupied by pure mercury. G. W. T.

Electromotive Force of Selenium. By S. KALISCHER (*Ann. Phys. Chem.* [2], **35**, 397—399).—The author points out that the method described in von Uljanin's paper (Abstr., 1888, 883) of preparing selenium sensitive to the production of E.M.F. by the action of light had been described by him two years ago (Abstr., 1887, 693). He states that in the paper by Fritts, quoted by von Uljanin as well as by himself, there is no question of an E.M.F. caused by the exposure of selenium to light, as he had already pointed out. Righi, in a recent paper, states that he has obtained a current from a selenium cell in the dark, and suggests that the reason that other observers have not noticed this is that they have attributed the whole E.M.F. to the action of light. Kalischer states that he had tried to obtain an effect of this kind, but without result, and he says that it does not appear from Righi's description that daylight was totally excluded in his experiments. He points out, moreover, that the method of observation of the effect of light would preclude any interference from such an effect if it existed, and that the E.M.F's. observed are therefore entirely due to light, and not the resultants of these and of effects of the kind which Righi states that he has obtained. G. W. T.

Irreciprocal Conductivity. By W. W. H. GEE and H. HOLDEN *Phil. Mag.* [5], **26**, 126—149).—Currents up to a given strength can be passed through strong sulphuric acid, but on attempting to pass a stronger current, the decomposition nearly ceases. The size of the electrodes has a considerable influence. If a current be passed from a large to a small electrode and then reversed, the current is almost completely arrested. The obstruction after reversal is at the anode, for if the cathode be exchanged for a large plate, the resistance is not removed, whilst if the anode be changed the current again passes. If the anode be increased, a greater current is required to produce insulation. Tables are given showing the current density at the anode required to give insulation under different conditions. The insulating condition is due to a resistance at the anode, and may conveniently be regarded as due to a film of badly conducting material. The film disappears very quickly if the current is broken, and instantly if it is reversed; the film is also removed by wiping. The film cannot be produced if the acid contains more than 70 per cent. of water. With increase of temperature, increase of current is required to produce insulation. Swan lamp filaments gave the same results as platinum, but other forms of carbon were disintegrated. Films could not be obtained with phosphoric or nitric acids, nor with potassium hydroxide. Solutions of soap did not give films, but a solution of sodium benzoate showed irreciprocal conductivity exactly like solid soap. The formation of the resisting film is probably due to the concentration of the acid at the anode, the oxygen under the above conditions becoming entangled in the film. An upper limit has been found at which the disturbing effect of the oxygen again comes into play. H. K. T.

Apparatus for determining the Conductivity of Electrolytes. By W. OSTWALD (*Zeit. physikal. Chem.*, **2**, 561—567).—A description of the modification of Kohlrausch's apparatus, which the author has found most useful, and also of a thermostat for work at constant temperature. H. C.

Specific Heats at High Temperatures. By W. SUTHERLAND (*Phil. Mag.* [5], **26**, 298—305).—The author has recalculated the results of Hirn's experiments (*Ann. Chim. Phys.* [4], **10**) on the specific heats of alcohol, ether, carbon bisulphide, and carbon tetrachloride at high temperatures from the experimental data, and obtains formulæ agreeing closely with those of Regnault at low temperatures. Hirn used an empirical formula connecting the times and temperatures, and then got the rate of cooling by differentiation. The values for alcohol at high temperatures obtained as above do not join on continuously with those of Regnault, hence there must be a point of inflection (at 50—80°) in the curve. This agrees with the point of inflection observed by Regnault at 70—80° in the total heat curve for alcohol.

The author has also found that the supposed inaccuracy of Regnault's specific heats of water at high temperatures (Velten, *Ann. Phys. Chem.* [2], **31**) does not exist. A single column of data (weight of hot water) has been wrongly copied out, whilst the results are correctly calculated from the data. H. K. T.

Specific Heats of Saline Solutions. By E. MATHIAS (*Compt. rend.*, **107**, 524—527).—The specific heat of any saline solution in which the number of equivalents, n, of the solvent is at least 25 for each equivalent of the substance dissolved, is accurately represented by the expression—

$$\gamma_n = \frac{a+n}{b+n}c,$$

c being the specific heat of the solvent, whilst a and b are constants. Two experiments are sufficient to determine the value of these constants. If e is the equivalent of the solvent we may take $\gamma_0 = ac/b$ and $E = eb$, and the first expression then becomes—

$$E\gamma_0 + nec = \gamma_n(E + ne),$$

that is to say, when a saline substance forms a dilute solution, Wœstyn's law is applicable to the solution, and it would seem as if the dissolved substance had acquired in the liquid state a new equivalent E, and a new specific heat γ_0, both of which are independent of the degree of dilution. C. H. B.

Heat of Combustion of Acids of the Oxalic and Lactic Series. By Louguinine (*Compt. rend.*, **107**, 597—599).—The determinations were made by means of the calorimetric bomb:—

	Per gram.	Per gram-molecule.	Difference.
Malonic acid......	2006·05 cal.	208650 cal.	147434 cal.
Succinic acid.....	3017·7 „	356089 „	155583 „
Pyrotartaric acid..	3876·3 „	511672 „	160246 × 3 cal.
Suberic acid......	5703·5 „	992409 „	151629 × 2 „
Sebacic acid......	6414·2 „	1295668 „	

The difference between oxalic and malonic acids is 148650 cal., and it would seem that oxalic, malonic, and succinic acids form one truly homologous series, and suberic and sebacic acids another, whilst pyrotartaric acid occupies an anomalous position, and probably differs from the others in constitution. The conversion of itaconic acid and its isomerides into pyrotartaric acid by hydrogenation, and the analogous conversion of fumaric and maleic acids into succinic acid, would develop about +34000 cal. in each case. The differences between the heats of combustion of homologues in the series of alcohols and hydrocarbons are not so regular as in the series of acids.

The heat of combustion of hydroxyisobutyric acid is 473689 cal., and the difference between this and the heat of combustion of lactic acid (144189 cal.) is less than the usual difference between homologues, but hydroxybutyric acid is not a true homologue of lactic acid.

The accuracy of the determinations made with the calorimetric bomb makes it possible to determine the differences between the heats of combustion of isomerides of the same chemical function, whereas with the older methods these differences were within the limits of the experimental errors. C. H. B.

Heats of Combustion of some Organic Substances. By I. Ossipoff (*Zeit. physikal. Chem.* 2, 646—649).—The experiments were performed with Berthelot's calorimetric bomb. The heats of combustion of the following substances were found to be per gram-molecule—

	At const. vol.	At const. pressure.
Stilbene, $C_{14}H_{12}$	1771·704 Cal.	1773·331 Cal.
Nononaphthene, C_9H_{18}	1380·748 „	1383·188 „
Isononaphthene	1381·719 „	1384·159 „

Comparing the heats of combustion of the nononaphthenes with that of diamylene, 1579 Cal., it is found that the differences do not follow Berthelot's rule, that two consecutive homologues should differ in their heats of combustion by about 150 Cal. But with reference to the heat of combustion of amylene itself, 804·4 Cal., one-fourth of the difference, 579 Cal., would be in pretty good agreement with the rule. Since the calculated heat of combustion, according to the equation $C_9H_{18} + 27O = 9CO_2 + 9H_2O$ is 1476 Cal. ($C = 97$, $H_2 = 67$), the heats of formation of nononaphthene and of isononaphthene would be 92·81 and 91·84 Cal.

The following heats of combustion were also determined:—Sorbic acid, $C_7H_8O_2$, 728·950 Cal.; terebic acid, $C_7H_{10}O_4$, 789·210 Cal.; cinnamic acid, $C_9H_8O_2$, 1028·452 Cal.; atropic acid, $C_9H_8O_2$, 1042·586 Cal.

H. C.

Heat of Combustion of Camphoric Acids. By W. LOUGUININE (*Compt. rend.* **107**, 624—626).

	Per gram.	Per gram-molecule.
Dextro-camphoric acid	6202·9 cal.	1240580 cal.
Dextro-camphoric anhydride	6824·14 „	1241994 „
Lævo-camphoric acid (from feverfew)	6227·7 „	1245540 „
Lævo-camphoric acid (from valerian)	6211·3 „	1242260 „
Racemo-camphoric acid	6261·3 „	2504560 „

The conversion of camphoric acid into sebacic acid by hydrogenation should develop +14,000 cal. The combination of camphoric anhydride with water is accompanied by a very slight thermal disturbance, a result which explains the ease with which the acid is converted into the anhydride.

The heats of combustion and therefore the heats of formation of the dextrogyrate and lævogyrate acid are practically identical, but the heat of combustion of racemo-camphoric acid is 18440 cal. greater than the sum of the heats of combustion of the optically active varieties.

C. H. B.

Method of determining Vapour-tensions at Low Temperatures. By J. WALKER (*Zeit. physikal. Chem.*, 602—605).—Three sets of Liebig bulbs are employed, the first two containing the solution to be examined, and the third distilled water. These are connected with a U-tube, containing pumice moistened with concentrated sulphuric acid. The apparatus is kept at constant temperature, and air drawn through the whole for some time by means of an aspirator. The relative decrease in the vapour-tension, produced by the salt in the solution, is then equal to the loss in weight of the third bulb, divided by the increase in weight of the U-tube.

An experiment takes on an average about 22 hours. The weight of water absorbed by the sulphuric acid will then be from 1 to 3 grams, if the temperature is from 18° to 25°. Details of experiments with this apparatus show that it gives very satisfactory results. H. C.

Vapour-tensions of Alcoholic Solutions. By F. M. Raoult (*Compt. rend.*, **107**, 442—445).—From the author's previous experiments, he deduced the law that 1 mol. of any non-saline solid dissolved in 100 mols. of any volatile liquid reduces the vapour-tension of the latter by a constant fraction of its value; the mean value of the fraction being 0·0105 (Abstr., 1887, 207). This law was not applied to salts in aqueous solution, because of the disturbing influence of the more or less complete dissociation of the salt. It seemed not improbable, however, that this influence would disappear with other solvents such as alcohol. New experiments have shown that in the case of lithium bromide and chloride, calcium chloride, and sodium ethoxide, the reduction of the vapour-tension is not constant if they are regarded as existing in solution in the anhydrous condition. If, however, it is assumed that these salts exist in the liquid in the form of alcoholates of the same composition as those which crystallise from the solution, namely, $LiCl + 5EtOH$, $LiBr + 5EtOH$, $CaCl_2 + 3EtOH$, and $NaEtO + 3EtOH$, then the law holds good, at least in dilute solutions, for saline as well as non-saline substances, and the value of the fraction is 0·0104. C. H. B.

Water of Crystallisation of the Alums. By H. Lescœur and D. Mathurin (*Bull. Soc. Chim.*, **50**, 33—43).—Experiments made with pure potassium alum gave the following results:—(1) The saturated solution of alum at 20° has a maximum tension of about 15·4 mm., or 0·89 with regard to the tension of water, which explains why alum does not deliquesce; (2) alum (with 24 mols. H_2O) at 20° has a tension of 4·6 mm., or 0·265 with regard to the tension of water; (3) the addition of a trace of water (0·12 mol.) increases the tension very considerably, showing that the hydrate contains 24 mols. H_2O and not more. Observations were also made at 70° and 100°; at 100° a hydrate with 6 mols. H_2O is formed.

Similar experiments made with potassium chrome-alum show that there are two hydrates, the one with 24 mols., the other with 12 mols. H_2O. The latter is readily obtained by keeping the ordinary salt over sulphuric acid until of constant weight: it is a lilac-coloured powder which does not lose its colour at 75°.

Ammonium alum has two hydrates with 24 and 6 mols. H_2O respectively (compare Maumené, *Bull. Soc. Chim.*, **46**, 261 and 807; and de Boisseau, *Bull. Soc. Chim.*, **47**, 494). N. H. M.

Electrolytic Method of Liquefying Gases. By H. N. Warren (*Chem. News*, **58**, 127—128).—Strong hydrochloric acid is introduced into a combustion tube, bent at right angles, so as to cover two small platinum plates fused into the closed end of the tube; a plug of asbestos, saturated with concentrated sulphuric acid, is placed at the bend, the open and shorter arm is then fused up and immersed in a freezing mixture. On the passage of a current through the plates, gas is evolved and liquefies at the other end; but on removing the tube from the freezing mixture and discontinuing the current, the liquefied hydrogen chloride is re-absorbed by the water. The experiment may then be repeated. Other compound gases behave in a similar manner. When acidified water is decomposed in this apparatus, and a platinum plate covered with platinum-black has been fused in the short end, explosions occur there, at intervals, and small quantities of water form, containing hydrogen peroxide, and having an ozonised odour. With chromic acid and water, the blue oxide of chromium is obtained. The method has also been applied to the liquefaction of oxygen and hydrogen, and the latter is said to have been "decidedly liquefied."

D. A. L.

Compressibility of Hydrogen, Oxygen, Nitrogen, and Air at very High Pressures. By E. H. AMAGAT (*Compt. rend.*, **107**, 522—524).—The author's results at pressures approaching 3000 atmospheres differ considerably from those obtained by Natterer, the differences being variable both in direction and magnitude. As a rule, it was found that the pressure required to produce a given contraction of volume was much greater than that stated by Natterer. The following table gives the volume at 15°, under various pressures, of a mass of gas which occupied unit volume at 15° and 760 mm.:—

Atmospheres.	Air.	Nitrogen.	Oxygen.	Hydrogen.
750	0·002200	0·002262	—	—
1000	0·001974	0·002032	0·001735	0·001688
1500	0·001709	0·001763	0·001492	0·001344
2000	0·001566	0·001613	0·001373	0·001161
2500	0·001469	0·001515	0·001294	0·001047
3000	0 001401	0·001446	0·001235	0·000964

The following table gives the mean coefficients of compressibility between different limits of pressure:—

Pressure in atmos.	Air.	Nitrogen.	Oxygen.	Hydrogen.
750—1000	0·000411	0·000407	—	—
1000—1500	0·000268	0·000265	0·000258	0·000408
1500—2000	0·000167	0·000170	0·000160	0·000272
2000—2500	0·000123	0·000122	0·000115	0·000197
2500—3000	0·000093	0·000091	0·000091	0·000158

At very high pressures, oxygen, nitrogen, and air have practically the same coefficient of compressibility, and the value of this coefficient is of the same order of magnitude as in the case of liquids. Under 3000 atmos., the coefficient approaches closely to that of ether under normal pressure.

Adopting the usual coefficient of compressibility for glass, the sp. gr. of the four gases under 3000 atmos. referred to water as unity are—

	Oxygen.	Air.	Nitrogen.	Hydrogen.
Apparent	1·0972	0·8752	0·8231	0·0880
Real............	1·1054	0·8817	0·8293	0·0887

If the pressures are measured along the axis of abscissæ and the values of *pv* along the axis of the ordinates, the curves are almost right lines with a slight concavity towards the axis of the abscissæ.

C. H. B.

Isotonic Coefficient of Glycerol. By H. DE VRIES (*Ann. Agronom.*, **14**, 376—379).—By a method similar to that used in his previous researches (Abstr., 1888, 1153) the author finds the isotonic coefficient of glycerol to be 1·78, very near those of cane- and invert-sugar, and malic, citric, and tartaric acids, which lie between 1·88 and 2·02. The lowering of the freezing point, which has been shown by Raoult to be related to the isotonic coefficient, is 17·1° in the case of glycerol, and 18·5—19·5° in that of the other substances mentioned.

J. M. H. M.

Action of a Magnet on Chemical Action. By H. A. ROWLAND and L. BELL (*Phil. Mag.* [5], **26**, 105—114).—Two iron rods are embedded in insulating material, the point of one and the side of the other being laid bare by removing the insulation. The rods are placed in a beaker between the poles of an electromagnet, and connected with a galvanometer. They are acted on by various reagents. When perpendicular to the lines of force, no current is produced. When parallel, a current is produced, the sharp-pointed rod forming the negative element; soon afterwards reversal takes place. The direction of the current is independent of that in the magnet. Similar but much weaker effects are produced with nickel and cobalt. The action is greatest with substances which, like nitric acid, attack the iron without evolution of hydrogen. The reversal can be annulled by preventing motion in the liquid by means of gelatin or sand. The electromotive force varies from 0·0001 to 0·02 volt. The evolved hydrogen probably acts mechanically in reducing the current. The protection of the pointed end from the reagents is due to the increased energy required to remove the iron in opposition to magnetic attraction. No differential action is observed with plane surfaces, but where a point occurs, protection ensues, and the elevation increases in size.

H. K. T.

Accelerating and Retarding Influences in Chemical Processes. By W. MEYERHOFFER (*Zeit. physikal. Chem.*, **2**, 585—601).—The reaction $HBrO_3 + 6HI = HBr + 3H_2O + 6I$, which was studied by Ostwald, was observed to form an exception to the ordinary rule of mass action. The author has, therefore, further investigated this reaction, and the accelerating and retarding influence which certain acids and salts are found to exercise on it. He finds that the exception alluded to is due to a retarding influence set up by the liberated iodine, which, at any moment, is directly proportional to the amount of free iodine present. When a certain point is reached, the solution becomes saturated with iodine, which then separates in the solid form, again interfering with the regularity of the reaction. Allowing for these influences, it is possible to interpret the numbers given by Ostwald for the acceleration caused by different acids. The author further studies the influence of ferric salts in accelerating the reaction. He finds that in the action of both ferric chloride and bromide on hydriodic acid, iodine is liberated in quantity rapidly attaining a maximum, and proposes to make further special experiments of this nature in order to obtain some idea of the various influences at work during the reaction. H. C.

Nitration of Benzene. By J. GIERSBACH and A. KESSLER (*Zeit. physikal. Chem.*, **2**, 676—714).—This paper contains the results of a large number of experiments carried out under L. Meyer's direction, with the object of studying the nitration of benzene as one of the non-reversible chemical changes. Nitric acid of all strengths was employed, the solution in the case of the stronger acids being diluted with nitrobenzene in order to moderate the action and admit of the change being studied as a time reaction. The results prove beyond doubt that the nitration of benzene does not follow the ordinary law of mass action. Instead of the most favourable proportions for the reaction being those of equivalent quantities of benzene and nitric acid, it is found that, in any time, the more benzene there is in solution, the less nitrobenzene will be formed, or in other words, that the benzene exercises a retarding influence on the reaction. This influence is so great that if nitric acid be mixed with equivalent quantities of benzene and nitrobenzene, only 2 per cent. of the acid will be found to act in the same time that 20 per cent. would undergo change if only a fourth or fifth part of the benzene were employed.

Since the velocity of the reaction is found to be proportional to the square of the amount of nitric acid employed, it might be assumed in explanation of the above that nitration is caused not by the action of the acid, but by that of the anhydride. Two equivalents of acid would then be required to one of benzene, since $2HNO_3 = H_2O + N_2O_5$, and the reaction would be still further retarded by the water formed during nitration.

It is found that the admixture of an equivalent of water with the acid does not so greatly retard the action as the addition of an equivalent of nitrobenzene, but a comparison of equal volumes shows that the retarding influence of water is a much greater one than that of the nitrobenzene. H. C.

The Foundations of Chemistry. By T. S. HUNT (*Amer. Chem. J.*, **10**, 333—356).—The relations of gaseous, liquid, and solid species to temperature and pressure, together with the phenomena of allotropism, specific gravity, hardness, and of chemical indifference, are briefly reconsidered: all of these properties the author maintains are intimately related to and dependent on a principle of condensation that he has enunciated on previous occasions, as in his "New Basis for Chemistry." He comes to the conclusion that something radically different from the "fantastic arrangements supposed by the present highly complicated atomic hypothesis" must be devised before we can hope to explain adequately the dynamical and chemical history of matter, and that signs are not wanting that this hypothesis so generally accepted since Dalton's time, is felt by many to be no longer adequate, and is doomed to the same fate as the corpuscular, and seemingly also the undulatory theories of light. H. B.

Method of determining Molecular Weights by Reduction of the Freezing Point. By E. BECKMANN (*Zeit. physikal. Chem.*, 2, 638—645 and 715—743).—The first part of the paper is devoted to a description of the apparatus and method of experimenting, the author laying particular stress on the necessity of an air-jacket between the cooling apparatus and the vessel containing the solution, and also on the advisability of using a thermometer divided into hundredths of a degree. The substances examined were all organic, and, where possible, solutions in the three solvents, water, acetic acid, and benzene, were taken, the effect of varying the concentration of each solution being also studied.

An examination was made of a number of carbonyl and oximido-compounds. The former gave in all three solvents numbers agreeing very well with the theoretical for the molecular weights, the results being most accurate for the more dilute solutions. The oximido-compounds gave molecular weights varying very largely with the concentration of the solutions, the concentrated solutions in some cases giving double the molecular weight of the more dilute. This appears to point to the formation of double molecules of these compounds in concentrated solutions.

Chloral anhydride, hydrate and alcoholate, and acetal were examined in all three solvents. In benzene, normal values are obtained, as also for the hydrate and acetal in water. Acetic acid appears to effect a partial dissociation of the last three compounds; water converts the anhydride into the hydrate, and splits the alcoholate into its components. Aldehyde-ammonia, which is insoluble in benzene, is completely dissociated by acetic acid, but in water it gave a molecular weight three times greater than that ordinarily assumed, which remained practically constant for all concentrations examined.

A series of alcohols, phenols, and acids examined in benzene gave numbers altogether at variance with the commonly accepted molecular weights for the more concentrated solutions, ethyl alcohol in 32·45 per cent. solution giving, for instance, 318. The more dilute the solutions, however, the nearer do the numbers approximate to the true molecular weights. It appears, moreover, that the above behaviour is due to the presence of the hydroxyl group, for on displacing this by an alcohol or acid radicle, normal values are obtained in benzene for the compounds formed. The above irregularities also disappear if acetic acid is used as the solvent instead of benzene. The values for the molecular weights are then approximately normal, suffering only a slight increase with rising concentration. The bimolecular polymeride of ethyl cyanide, $(C_3H_5N)_2$, also exhibits irregularity in benzene, but in acetic acid it gives numbers agreeing with the above formula.

A few aromatic compounds were examined in benzene and acetic acid, and gave normal values.

Discussing the results obtained with varying concentrations, from the fact that the molecular weight is almost always found to rise with the concentration, the author concludes that the molecules of the dissolved substance exercise an attraction on one another as they are brought into closer contact. It is also probable that in most cases some action occurs between the molecules of the dissolved substance and the solvent. In accordance with the proposal of Arrhenius, the author also calculates the molecular weight from the depression given by one gram of substance in 100 c.c. of the solvent, instead of 100 grams. He finds that by so doing the effect of increasing concentration is much reduced. Another source of error is that, taking Van't Hoff's expression for the reduction of the freezing point (Abstr., 1888, 780), $0·02\ T^2/W$, as the concentration rises, T decreases, and therefore also the value of the above expression, which effects an increase in the molecular weight. This is, however, in part balanced by a simultaneous decrease in W, the latent heat of fusion of the solvent.

In using the cryoscopic method of determining molecular weights, water should on account of its dissociative properties only be used as solvent in the case of non-conductors. Benzene and other indifferent solvents, such as nitrobenzene, ethylene dibromide, and naphthalene, cannot be used in the case of hydroxyl compounds or substances with acid properties. The solvent of most general application, and the one to be chiefly recommended, is acetic acid. The concentration of the solution should, if possible, be such as to give a reduction of 1° to 2°, but it is very advisable to take observations for a number of different concentrations.

H. C.

Resistance to Light of Colouring Matters fixed in Tissues. By J. Joffre (*Bull. Soc. Chim.*, **49**, 860—862).—In examining the influence of light on coloured materials, certain precautions must be taken to render the experiments trustworthy. For example, a sample of material dyed with a very unstable colour; the fibres being completely saturated with the dye, might attain a shade which would offer a certain resistance to sunlight; in such a case it would be inferred that the dye was stable. If, however, the sample is compared with a material dyed by some other colouring matter, the proportion of dye in the fibre being the same in both, and transparent shades being employed, the instability of the sample would be at once perceptible.

It is equally essential that the two exposures should be simultaneous, not only because sunlight varies in intensity, but also because the condition of the atmosphere may influence the results. Of two samples of material exposed to the same light, one of which is placed in moist, the other in dry air, the former will lose its colour far more quickly than the latter.

F. S. K.

Apparatus for Fractional Distillation in a Vacuum. By S. B. Newbury (*Amer. Chem. J.*, **10**, 362—363).—The distilling flask is fitted with a stoppered separating funnel, whose drawn-out end reaches almost to the bottom of the flask; it serves to admit a very small but constant current of air to stop bumping, and also to introduce fresh fractions into the flask. Between the condenser and the receiver is another stoppered separating tube, which enables the receiver to be changed without admitting air to the whole apparatus. H. B.

Inorganic Chemistry.

List of Elementary Substances announced from 1877 to 1887. By H. C. Bolton (*Chem. News*, **58**, 188).—The names of 58 substances, announced as being elementary, together with their sources and the names of their discoverers, are given in tabular form.

Chlorine and Cyanogen. By E. Allary (*Bull. Soc. Chim.*, **49**, 865—867).—The author cites the isomorphism of potassium chloride and potassium cyanide as fresh evidence in support of the views of Brodie, Dumas, Lockyer, and others that chlorine is composed of two elements. If the atomic weight of chlorine is divided into two parts proportional to the atomic weights of carbon and nitrogen, the two constituents of chlorine would have the atomic weights 19·1 and 16·4 respectively. From the study of certain series of organic compounds, Dumas came to the conclusion that chlorine consists of two elements, the atomic weights of which are 19 and 16·5 respectively. If this view were correct, chlorine would probably be composed of fluorine and oxygen, and the oxygen is perhaps intimately united with $\frac{H}{2}$. Meyer's observation that oxygen is produced when chlorine is strongly heated, may be adduced in support of this theory.
F. S. K.

Apparatus for a Constant Supply of Chlorine. By A. Vosmaer (*Zeit. anal. Chem.*, **27**, 638—640).—The manganese dioxide is used in fragments of the size of peas, and is placed in a two-necked bottle, at the bottom of which there is a layer of broken glass or pumice. This stands in a water-bath. Hydrochloric acid is supplied from a reservoir at a higher level by a tube reaching to the bottom of the layer of glass, a T-piece and stopcocks allowing the same tube to serve for the removal of the manganese solution. The corks should be soaked in paraffin. Suitable drying apparatus can be attached, and will not require replenishing for a long time. The chlorine begins to come off when the temperature of the bath reaches 50°, and by means of a stopcock on the outlet its rate is completely under control. The evolution can speedily be arrested by closing the stopcock at the outlet of the drying apparatus and emptying the water-bath. The apparatus is then left full of chlorine, and is ready at any moment to give a supply of the gas completely free from oxygen.
M. J. S.

Dissemination of Sulphur and Phosphorus in Masses of Metal. By H. N. Warren (*Chem. News*, **58**, 177—178).—When sulphur is well mixed with excess of molten iron, and a rod cast from the mass is made the positive electrode of an electric circuit, in a bath of ferrous chloride, with a platinum or copper negative electrode, the metallic iron is dissolved and is precipitated on the negative electrode, whilst ferrous sulphide, FeS, remains attached to the positive electrode. In the same way, iron phosphide, Fe_4P, may be separated from a mass of the metal. Other metals of the iron group behave in a similar manner. The author regards the above compounds, FeS, Fe_4P, and the compound Fe_2Si, obtained by him, as the lowest forms of the respective iron sulphides, phosphides, or silicides, although ordinary analytical results may indicate still lower forms, owing to the intimate dissemination of these compounds throughout the mass of the metal. The sulphides of the metals of the second group are not disseminated in this way through the mass of the metal (compare Abstr., 1888, 555—556). D. A. L.

Preparation of Hydrogen Iodide. By A. ÉTARD (*Bull. Soc. Chim.*, **49**, 742—743).—In preparing hydrogen iodide from iodine and amorphous phosphorus, the author places the iodine in a flask provided with a bent neck and connected with the vessel containing the phosphorus and water by means of a bent tube. By turning the flask round the bent tube, fresh quantities of iodine can be added when requisite without admitting air into the apparatus. F. S. K.

Hydrogen Sulphide Apparatus. By J. H. J. DAGGER (*Chem. News*, **58**, 127).—The apparatus figured and described consists of two glass globes connected by india-rubber tubing. The acid is put in one of the globes, the ferrous sulphide (zinc or marble) in the other; they are fitted with tubes and corks and then fixed in a suitable position. D. A. L.

Apparatus for the Preparation of Hydrogen Sulphide. By P. CHANTEMILLE (*Bull. Soc. Chim.*, **50**, 170—171).—The iron sulphide is contained in an épouvrette, and the acid in an ordinary flask fitted with a doubly-bored cork, through the one hole of which is passed a tube reaching to the bottom of the flask, and closed at its upper end by an india-rubber tube and pinch-cock; the second hole is fitted with a short tube bent at right angles and fitted to the lower end of the épouvrette. The force of gas is increased or diminished by raising or lowering the flask. The gas is purified in the usual manner.
N. H. M.

Chydrazaïne or Protoxide of Ammonia. By E. J. MAUMENÉ (*Bull. Soc. Chim.*, **49**, 850—853).—*Chydrazaïne* is evolved when a solution of potassium permanganate (158 grams) and sulphuric acid (40 grams SO_3) is added to dried, crystallised ammonium oxalate (141·2 grams), the whole well mixed and gently heated until it begins to boil. The gaseous product is absorbed in hydrochloric acid and a neutral solution of the salt can thus be obtained. The *hydrochloride* is crystalline and very readily soluble in water, but only sparingly in alcohol. The sublimed salt has the composition $N_2H_8O,2HCl$, but the crystals dried by means of the anhydrous salt contain one-fifteenth of their weight of water. When a solution of the hydrochloride is mixed with platinic chloride, a *platinochloride* is obtained, the composition of which varies with the conditions of the experiment; with excess of the hydrochloride, a yellow salt is formed, the composition of which is approximately N_2H_6O,H_2PtCl_6, but if excess of platinic chloride is added, the proportion of platinum is sensibly increased. The *sulphate* is crystalline and soluble in water, but only very sparingly so in absolute alcohol; it forms a double salt with aluminium sulphate. The *nitrate* is crystalline. When a solution of the nitrate is evaporated, nitric acid, nitric peroxide, nitrogen, and a compound having the composition N_2H_2 are evolved.

F. S. K.

Action of the Electric Spark on Mixtures of Nitric Oxide with Hydrogen, with Methane, &c. By S. COOKE (*Chem. News*, **58**, 130—131).—Under the influence of sparks (from a coil capable of giving a 4-inch spark), with the eudiometer wires half an inch apart, a mixture of hydrogen and nitric oxide always explodes, provided the proportion of hydrogen to nitric oxide does not exceed 6 : 10; but with the wires closer together, or with a feeble coil, or if the pressure is diminished to 300 mm. of mercury, no explosion occurs. The carefully dried gases explode quite as readily as when they are not dried. The nature of the gaseous mixture after explosion varies very considerably, but there is little doubt that much of the nitric oxide is converted into oxygen and nitrogen. Explosions have also been obtained with nitric oxide and hydrogen sulphide; with nitric oxide and methane with the production of carbonic anhydride and oxygen: other hydrocarbons in proper proportions and suitable spark make an explosive mixture with nitric oxide. Carbonic and nitric oxides mixed do not explode under the influence of the spark, but combination goes on gradually with the production of carbonic anhydride and nitrogen.

D. A. L.

Decomposition of Nitric Oxide in Contact with Water and with Potash. By S. COOKE (*Chem. News*, **58**, 155—156).—Nitric oxide exposed in tubes over water in the dark undergoes gradual decomposition with the production of nitrous acid, nitrogen, and a little nitrous oxide. The change is always slow, but is more active at the commencement than at the end of an experiment; it is also accelerated by the presence of platinum and by heat, whilst admixture with hydrogen retards it. The action of potassium hydroxide on nitric oxide is also aided by platinum and heat (compare this Journal, 1877, ii, 37).

D. A. L.

Action of Hydrogen Sulphide on Arsenic Acid. By L. W. MCCAY (*Zeit. anal. Chem.*, **27**, 632—634; compare Brauner and Tomiček, Trans., 1888, 145).—When a slow stream of hydrogen sulphide is passed through an acidified solution of an arsenate at 70°, besides arsenic pentasulphide there is also formed some free thioxyarsenic acid, H_3AsO_3S. This, under the influence of mineral acids and heat, decomposes into free sulphur and arsenious acid, the latter of which then yields arsenic trisulphide with the hydrogen sulphide. A solution of thioxyarsenic acid may be obtained by passing hydrogen sulphide not in excess into a cold, dilute, acidified solution of potassium arsenate. If a larger quantity of hydrogen sulphide is employed, the excess may be removed either by immediate addition of copper sulphate or by a vigorous stream of air bubbles. An opalescence caused by free sulphur may be removed by shaking with asbestos. The clear, strongly acid liquid obtained, exhibits the following properties. It remains clear for a long time after addition of sulphuric or hydrochloric acid; it gives no immediate precipitate with hydrogen sulphide, but ultimately yields one. When boiled, it gives a precipitate of pure sulphur, without evolution of hydrogen sulphide or sulphurous anhydride. With hydrogen sulphide, the boiled and cooled liquid gives an immediate precipitate of arsenic trisulphide; it gives no precipitate with copper sulphate; with mercuric chloride it gives immediately a heavy yellowish-white precipitate; with silver sulphate it gives a heavy black precipitate, the filtrate from which contains no arsenious acid. The potassium thioxyarsenate of Bouquet and Cloëz agrees with this solution in all the above particulars.

M. J. S.

Barium Sulphite. By E. R. HODGES (*Chem. News*, 58, 128); G. S. JOHNSON (*ibid.*, 155).—Hodges' experiments led him to infer that barium sulphite is insoluble in hydrochloric acid; but Johnson proves it to be readily and completely soluble in that solvent. He, moreover, shows that pure aqueous barium chloride is not precipitated by sulphurous acid, but that in the presence of dissolved oxygen a precipitate of barium sulphate forms. D. A. L.

Solubility of Gypsum. By G. A. RAUPENSTRAUCH (*Chem. Centr.*, 1888, 821—822, from *Pharm. Centralhal.*, 29, 229—233).—The author finds that a saturated solution of gypsum is readily obtained, but supersaturation of the solution can only be obviated by shaking the solution for some time. The solubility of gypsum increases up to the temperature of 32°, between 32° and 38° it remains almost constant, and at higher temperatures than 38° decreases. Natural gypsum comports itself like artificial, provided it be pure. After heating, gypsum takes up water of crystallisation more or less rapidly, and shows the normal solubility again. J. W. L.

Ancient Mortar from a Roman Wall in London. By J. SPILLER (*Chem. News*, 58, 189).—While examining some mortar from a Roman wall, exposed when sinking the foundations of the new Post Office buildings in St. Martin's-le-Grand, the author found, after extracting as much silica as possible by means of dilute hydrochloric acid, that the residue yielded nearly 11 per cent. of silica to cold dilute sodium hydroxide. Under similar treatment with cold soda, builder's sand and pulverised flints yield a mere trace of silica in solution, whilst mortars 20, 100, and many hundreds of years old yielded quantities of silica increasing with the age of the mortar. The author suggests that perhaps the Romans used a puzzuolana in compounding their mortar, or perhaps this soluble silica or silicate is the direct result of long contact of plain sand and lime. The mortar from St. Martin's-le-Grand had the following composition per cent.:—Sand and brick, 46·48; acid-soluble, SiO_2 0·52; alkali-soluble, SiO_2 10·44, Al_2O_3 3·00, Fe_2O_3 0·48, CaO 20·02, MgO 0·76, CO_2 13·03, SO_3 0·37, NaCl trace, H_2O and loss 4·90. D. A. L.

Analysis of Money. By J. C. WELCH (*Chem. News*, **58**, 164—165).—The author has analysed some specimens of "manilla money" made in Birmingham. It is yellowish-red, reddish-yellow, brass or bronze-like in colour, and in shape like a G. They proved to be variable alloys of lead and copper with small quantities of iron, tin, zinc, antimony, and arsenic. Some contained pieces of originally unmolten metal, and some had a semi-fused appearance. Another coin resembling gold in colour contained per cent.: Cu, 62·58; Zn, 37·26; Fe, 0·11; Pb, 0·013, and had been silvered to pass for a *6d.*-piece. D. A. L.

New Hydrated Cupric Chloride. By E. CHUARD (*Chem. Centr.*, 1888, 887, from *Arch. sci. Phys. Nat. Genève* [3], **19**, 477).—A hydrated cupric chloride of the formula $CuCl_2 + 3H_2O$ crystallises from the solution of the green hydrate when cooled down to 0°. The existence of this compound explains the change in the colour of the solution which takes place when it suffers dilution, for the chloride of the green hydrate contains only 2 mols. H_2O, and by diluting or by cooling below 0°, the chloride with 3 mols. H_2O is formed, and gives a blue colour to the solution. The latter chloride again loses 1 mol. H_2O when the solution is boiled. J. W. L.

Purification of Mercury. By J. M. CRAFTS (*Bull. Soc. Chim.*, **49**, 856—860).—Mercury can be completely freed from lead, zinc, tin, and other impurities by placing it in a slightly inclined glass tube provided with a funnel at the lower extremity, and aspirating a gentle stream of air through the apparatus for about 48 hours. The oxides of the metals collect at the upper end of the tube, and after about 24 hours, as a rule, the surface of the mercury is quite clean and the operation is finished. Large quantities can be treated in this way, but mercury which has been used for amalgamating zinc contains such a large amount of impurity that this method cannot be suitably employed. Silver is not removed by this process.

A stream of pure air was passed through pure mercury contained in the apparatus described above, but even after 10 days' time no appreciable quantity of oxide was formed.

Platinum, in the form of thin foil, is not attacked by cold mercury, but when the latter is boiled, air being excluded, the platinum is gradually acted on. Only a small quantity is dissolved, as a large proportion separates in the form of a black powder, and almost the whole is simply held in suspension. The surface of the mercury remains bright, but when a stream of air is passed, the platinum collects at the surface after some time as a black powder, and on distilling the separated mercury only a very small quantity of platinum remains. F. S. K.

The average of the 26 results obtained by the electrolysis of the ammonium and potassium double salts is higher than the average of all the results. This is probably due to the fact that in oxidising the tin, the platinum vessel is always attacked to a slight extent, and that in dissolving the stannic bromide, a small portion may be lost by volatilisation. If, therefore, the average of the 26 experiments is taken as the most trustworthy result, the atomic weight of tin is 118·8034 ($O = 15·96$) or 119·1 ($O = 16$).

Experiments in which it was sought to determine the atomic weight by converting pure tin into stannic sulphide, and estimating the sulphur in the latter, did not give satisfactory results (118·676 as the average of eight experiments). It was also found that when the oxide is reduced with pure hydrogen, a small quantity of tin is always volatilised. F. S. K.

Action of Incandescent Platinum Wire on Gases and Vapours. By W. R. Hodgkinson and F. K. S. Lowndes (*Chem. News*, **58**, 187).—When a spiral of platinum wire is exposed to the action of chlorine in a glass globe and rendered incandescent by an electric current, a white glow is observed round the heated wire, the sides of the globe become covered with platinous chloride, and very fine crystals of platinum are formed on the wire. With bromine or iodine vapour, the flame round the wire is greatly increased, but only a very small quantity of platinous bromide or a trace of the iodide is formed, and no crystalline metal is produced. With dry silicon fluoride, crystals of silicon are deposited, and the top of the globe is deeply corroded, presumedly by the liberated fluorine. D. A. L.

Normal Platinum Chloride. By R. Engel (*Bull. Soc. Chim.*, **50**, 100—102).—Normal platinum chloride, $PtCl_4 + 4H_2O$, can be obtained by dissolving the calculated amount of platinum oxide in a solution of platinum chloride hydrochloride; the liquid is filtered and evaporated. The crystals are deliquescent like those of the hydrochloride. When dry hydrogen chloride is passed over the crystals heated at 50°, the hydrochloride is formed; at a lower temperature no combination takes place. N. H. M.

Mineralogical Chemistry.

Hexagonal Zinc Sulphide. By W. Stahl (*Chem. Centr.*, 1888, 943, from *Berg. Hütt. Zeit.*, **47**, 207—208).—The naturally occurring mineral, wurtzite, which has also been artificially prepared, has been noticed by the author as a product of the blast furnace of the Sophia smelting work in the Lower Harz. It forms clear, wine-yellow, shining, hexagonal crystals, mostly in tufts, with the faces $\infty P2$, $P2$, $2P2$, and $0P$. Cleavage in the direction R and ∞R. Hardness = 3—4, sp. gr. = 4·32; composition:—

Zn.	Fe.	Mn.	Pb.	S.
66·08	0·55	trace	0·31	32·88 = 99·82

J. W. L.

Arsenopyrite from Servia. By A. Schmidt (*Zeit. Kryst. Min.*, **14**, 573—574).—The specimen examined formed part of the collection of the Royal Hungarian Geological Survey at Budapest. It is stated to have come from the Luta Strana adit-level, Servia. The arsenopyrite occurs, with iron pyrites and zinc blende, in small prismatic crystals, on which were observed the forms ∞P, $0P$, $\frac{1}{24}\breve{P}\infty$, $\frac{1}{6}\breve{P}\infty$, the two last being new for this mineral. The axial ratio is computed to be $a : b : c = 0·686 : 1 : 1·170$. Analysis of this arsenopyrite gave the following results :—

Fe.	As.	Sb.	S.	Zn.	Insoluble.	Total.
34·58	42·38	0·14	21·71	0·46	0·22	99·49

The percentage of zinc is evidently due to an unavoidable admixture of blende. B. H. B.

Formation of Deposits of Oxides of Manganese. By F. P. Dunnington (*Amer. J. Sci.*, **36**, 175—178).—In view of the results of a series of 15 experiments, it appears possible that many deposits of manganese ore in calciferous rocks have been formed by the action of solutions of sulphates rather than of bicarbonates. An illustration of such action is perhaps afforded by the manganese deposits of Crimora, Augusta Co., Virginia. Wherever pyrites has been deposited, the outcrop is gradually converted into limonite by weathering, and the acid solution of ferrous sulphate which sinks into the underlying deposits, must carry with it all the manganese in the pyrites itself, and in any disintegrating silicates. As this solution is exposed to the air or meets with calcium carbonate, ferrous carbonate will be formed, whilst the manganese sulphate will remain in solution until exposed to the action of both air and calcium carbonate at the same time.

B. H. B.

Artificial Production of Hydrocerusite. The Composition of this Mineral and the Constitution of White Lead. By L. Bourgeois (*Bull. Soc. Chim.*, **50**, 83—85).—Hydrocerusite, $2PbCO_3, Pb(OH)_2$, is formed if a boiling solution of lead acetate (1 mol.) is treated with litharge ($1\frac{1}{2}$ mol.), and when cold, with carbamide (1 mol.). The liquid is then filtered and heated at about 130° for some hours, when a quantity of nacreous spangles separate which are washed with water. These have a sp. gr. = 6·14 at 15°, dissolve with effervescence in nitric and acetic acids, and give off water and carbonic anhydride at 400°, leaving a residue of massicot slightly coloured by a trace of minium.

White lead consists of a mixture of hydrocerusite and cerusite.

N. H. M.

Preparation of Pyromorphite and Mimetesite. By L. Michel (*Zeit. Kryst. Min.*, **14**, 619, from *Bull. soc. franç. min.*, **10**, 133).—The author mixes three equivalents of lead phosphate or arsenate, or a mixture of the two, with one equivalent of lead chloride in a porcelain crucible. He covers the mixture with a thin layer of lead chloride, and places the crucible in one of fireclay. Both are hermetically sealed, the intermediate space being filled with ignited magnesia. The crucibles are then heated to the melting point of gold, and slowly cooled. The cavities of the fused mass contain hexagonal prisms as much as 2 cm. in length and 1 mm. in width. The best results were obtained with the mixture corresponding with kampylite (Analysis 4), the prisms being well developed and perfectly transparent. The crystalline products obtained had the following compositions:—

	$Pb_3As_2O_8$.	$Pb_3P_2O_8$.	$PbCl_2$.	Total.	Sp. gr.
1	89·75	—	9·92	99·67	7·12
2	84·73	4·97	10·03	99·73	6·93
3	79·85	10·06	8·98	98·89	6·97
4	69·78	20·02	10·07	99·87	6·93
5	46·05	44·87	9·79	100·71	—
6	29·37	59·24	10·31	98·92*	—
7	19·43	68·98	10·12	98·53	—
8	10·21	79·67	9·71	99·59	—
9	—	89·87	10·14	100·01	—

On the addition of a small quantity of lead chromate, yellow or orange crystals are obtained. In rare cases, they are of a grass-green colour.

B. H. B.

Uranite from Madagascar. By E. JANNETTAZ (*Zeit. Kryst. Min.*, **14**, 608, from *Bull. soc. franç. min.*, **10**, 47).—The mineral examined forms greenish-yellow aggregates of crystals exactly similar in appearance to those of Autun. Analysis gave the following results:—

H_2O.	P_2O_5.	UO_3.	Fe_2O_3.	CaO.	Total.
22·08	14·93	55·08	1·36	6·51	99·96

These results correspond with the formula $(UO_2,Fe,Ca)_3P_2O_8 + 12H_2O$. Of the proportion of water, 9 per cent. is evolved at 65°.

B. H. B.

Baryto-celestine from Werfen in Salzburg. By E. HATLE and H. TAUSS (*Jahrb. f. Min.*, 1888, ii, Ref., 210, from *Tschermak's min. Mitth.*, **9**, 227—231).—The baryto-celestine accompanying the wagnerite of Werfen has hitherto been regarded as barytes. It forms druses, crystals 1·5 cm. thick, and radiated or granular masses. It is of a pink colour, and translucent, with a hardness of 3·5 and a sp. gr. of 4·17. Analysis gave 84·80 per cent. of barium sulphate and 15·05 of strontium sulphate. The formula is $4BaSO_4 + SrSO_4$.

B. H. B.

Arseniopleite, a New Swedish Mineral. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, ii, Mem., 117—122).—Numerous rare and new minerals occur with braunite and hausmannite at the manganese mine, Sjögrufvan, in the parish of Gryhyttan, Oerebro, Sweden. In November, 1887, the author discovered there another new mineral,

* 99·51 in the original paper.

which he names *arseniopleite* from the metal arsenic, and πλεῖον (more). The mineral occurs in intimate association with rhodonite in small veins in dolomite. It also occurs in the same rock in masses 0·5 to 1 cm. in thickness. Its colour is cherry-red. No crystals have been found. It is uniaxial and positive, and judging from the cleavage appears to crystallise in rhombohedral forms. Analysis gave the following results:—

As_2O_5.	MnO.	Fe_2O_3.	PbO.	CaO.	MgO.	H_2O.	Total.
44·98	28·25	3·68	4·48	8·11	3·10	5·67	98·27

Traces of Sb_2O_5 and Cl were observed. Arseniopleite is a basic arsenate, like olivenite. It resembles most closely diadelphite and synadelphite. It, however, contains no alumina. Its relation to the other hydrated arsenates occurring in Sweden may be seen from the following list:—

Chondroarsenite....	$(MnO)_5As_2O_5 + 2\frac{1}{2}H_2O$.
Xanthoarsenite	$(MnO)_5As_2O_5 + 5H_2O$ (Abstr., 1886, 25).
Hæmafibrite	$(MnO)_6As_2O_5 + 5H_2O$.
Polyarsenite	$(MnO)_4As_2O_5 + H_2O$ (Abstr., 1887, 347).
Allactite	$(MnO)_7As_2O_5 + 4H_2O$.
Diadelphite........	$(MnO)_8As_2O_5 + Al_2O_3(Fe_2O_3) + 8H_2O$.
Synadelphite	$(MnO)_5As_2O_5 + Al_2O_3(Fe_2O_3) + 5H_2O$.
Arseniopleite	$3(MnO,CaO,PbO,MgO)_3As_2O_5 + Mn_2O_3(Fe_2O_3) + 3H_2O$.

(Compare Abstr., 1887, 902.) B. H. B.

Treatment of Natural Silicates with Hydrochloric Acid as a means of Ascertaining their Structure. By E. A. SCHNEIDER (*Amer. Chem. J.*, **10**, 405—408).—Referring to the recent paper by Clarke (Abstr., 1888, 659), the author remarks that the weathering of minerals may be used for drawing conclusions as to their constitution, and suggests the carrying out of a number of experiments, substituting hydrochloric acid for the atmospheric carbonic anhydride, and accelerating its action by heating in sealed tubes in a water-bath, the mineral being finely powdered. H. B.

Minerals of the Tyrol. By A. CATHREIN (*Jahrb. f. Min.*, 1888, ii, Ref., 220—221, from *Tschermak's min. Mitth.*, 8, 400—413).—1. *The so-called Paragonite from the Zillerthal.*—The composition of this mineral is found to be that of talc, and not that of mica. It is as follows:—

SiO_2.	MgO.	FeO.	H_2O.	Total.
62·24	30·22	2·66	4·97	100·09

This talc is the matrix of the actinolite from this locality.

2. *A New Pseudomorph of Fassaite.*—This was found at Monzoni in association with crystals of grossular remarkable for the occurrence of the rare plane $4O\frac{4}{3}$, first observed by Bauer on garnet from Oravicza. The composition of the fassaite is as follows:—

ville. Some of the crystals were 2 inches in length, and in perfection, depth of colour, and transparency, rival those from St. Gothard.

6. *Aragonite Pseudomorph.*—A crystal from Pima Co., Arizona, originally consisted of aragonite, but had been almost entirely changed and impregnated by ferric and manganese oxides. It had an outer coating of white cacholong. B. H. B.

Artificial Formation of Mica. By C. Doelter (*Jahrb. f. Min.*, 1888, ii, Mem., 178—180).—In May, 1888, the author announced to the Royal Academy of Sciences of Vienna, that he had successfully produced mica artificially. From alumina-hornblende and augite he obtained biotite, and from pennine and glaucophane he obtained phlogopite, when these minerals were fused with magnesium fluoride and sodium fluoride at a red heat. In the same manner, biotite is obtained on fusing the silicate, $K_2Al_2Si_2O_8 + Mg_2SiO_4$, with sodium and magnesium fluorides. When ferrous silicate is substituted for the magnesium silicate, ferriferous biotites are obtained. Recently the author has obtained very excellent results by fusing garnet and andalusite with fluorides. Biotite, closely resembling that from Vesuvius, is obtained by fusing pyrope or almandine with sodium and magnesium fluorides. Very beautiful crystals of muscovite are obtained by fusing andalusite with potassium fluoride, silicon fluoride, and aluminium fluoride in the proportion of 4 : 3 : 1 at a low red heat. Curiously enough, the artificial mica usually exhibits a smaller axial angle than the natural. Zinnwaldite is obtained by fusing, at a dull red heat, andalusite with 4 parts of potassium fluoride, 3 of silicon fluoride, 2 of aluminium fluoride, and 1 of lithium carbonate.

B. H. B.

Chiastolite. By M. Rohrbach (*Chem. Centr.*, 1888, 942, from *Zeit. deut. geol. ges.*, **39**, 632—638).—The author again points out that the characteristic cross-like division of the coal-black substance has no connection with a twin-formation, but most probably with a crystalline "growth" which, according to the author's view, has been brought about as follows:—The primarily-formed black, prismatic crystals have grown on the ∞P faces more than on the edges, and, consequently, appear notched; the black, slate-like particles covering the crystals are pressed back from the faces, but on the edges they become enclosed by the substance of the crystals.

J. W. L.

Cordierite-gneiss from Connecticut. By E. O. Hovey (*Amer. J. Sci.*, **36**, 57—58).—Cordierite (or iolite), which has hitherto been found in America only as an accessory constituent in rocks, has been found at Guildford, near New Haven, with biotite, quartz, and some plagioclase constituting a true gneiss. This is the first time cordierite-gneiss is reported from America. B. H. B.

Occurrence of Piemontite. By B. Koto (*Zeit. Kryst. Min.*, **14**, 599—600, from *J. Coll. Sci. Tokyo*, **1**, 303).—In a former paper, the author described the occurrence of piemontite (manganese-epidote) with glaucophane-bearing rocks of the archæan-schist series. The dark-violet rocks are developed most typically in the vicinity of the town of Tokusima, on the island of Shikoku. Here piemontite occurs in association with fine quartz grains, forming a stratified rock, in which sericite, garnet, rutile, orthoclase, and specular iron ore occur as accessory constituents. In the glaucophane-schists, piemontite also occurs as an accessory constituent. An analysis of piemontite, isolated by means of Thoulet's solution, from Otakisan in the province of Awa, gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	CaO.	MgO.	Na_2O.	H_2O.	Total.
36·16	22·52	9·33	6·43	22·05	0·40	0·44	3·20	100·53

Piemontite-schist is widely distributed throughout Japan. Like glaucophane-schist, it occurs in the lowest portion of the chlorite-sericite gneisses of the archæan formation. B. H. B.

Origin of Primary Quartz in Basalt. By J. P. Iddings (*Amer. J. Sci.*, **36**, 208—222).—The basalts in the vicinity of the Rio Grande Cañon, Tewan Mountains, New Mexico, contain porphyritic rounded grains of crackled quartz, surrounded by light green shells of microscopic augites. Similar remarkable occurrences of free silica in a basic magma are met with in the lithophysæ of the rhyolitic obsidian from Obsidian Cliff, Yellowstone National Park, and from Cerro de las Navajas, Mexico. This anomalous association of primary igneous materials was most probably brought about by great pressure and aqueo-igneous action, induced by the influence of water-vapour absorbed in the molten glass. In order to show that the chemical composition of quartz-bearing basalts is not characteristic of a particular modification of rock magma, the author gives the following analyses:—

	I.	II.	III.	IV.	V.	VI.
SiO_2	52·27	52·37	51·57	52·38	57·25	56·28
TiO_2	1·49	1·60	1·43	1·22	0·60	0·84
Al_2O_3	17·68	17·01	17·72	18·79	16·45	14·28
Fe_2O_3.......	2·51	1·44	6·24	2·88	1·67	4·69
FeO........	5·00	5·89	1·78	4·90	4·72	4·05
MnO.......	0·23	0·32	0·45	0·18	0·10	0·16
CaO........	8·39	7·59	8·82	7·70	7·65	7·94
MgO	6·05	6·86	4·91	4·91	6·74	6·37
BaO........	0·06	0·06	0·16	0·11	—	—
K_2O	1·58	1·59	1·99	1·76	1·57	1·23
Na_2O	4·19	3·51	3·59	3·99	3·00	2·98
Li_2O	—	—	—	—	—	0·01
H_2O	0·82	1·29	0·64	0·53	0·40	0·93
CO_2........	trace	0·37	0·58	—	—	—
P_2O_5	—	—	—	0·56	0·20	0·40
Cl..........	trace	trace	—	—	—	0·17
Total.......	100·27	99·90	99·88	99·91	100·35	100·28

B. H. B.

Peridotite of Iron Mine Hill, Cumberland, Rhode Island. By M. E. WADSWORTH (*Jahrb. f. Min.*, 1888, ii, Ref., 224—225, from *Bull. Mus. Comp. Zool. Harvard*, 7, 183).—The mean of a number of analyses of the iron ore, peridotite, from Iron Mine Hill, Cumberland, Rhode Island, was as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3 + FeO.	MnO.	CaO.	MgO.	TiO_2.
22·87	10·64	44·88	2·05	0·65	5·67	9·99

Zn.	H_2O.	Total.
0·20	(3·05)	100·00

Under the microscope, the ore is seen to consist of magnetic pyrites, olivine, plagioclase, and actinolite. B. H. B.

The Badenweiler Ore Deposit. By A. WOLLEMANN (*Zeit. Kryst. Min.*, **14**, 624—628, from *Verh. phys. med. ges. Würzburg*, **20**, 39).—The ore deposit of Badenweiler traverses a highly siliceous sandstone, and is enclosed on the one side by granite and porphyry and on the other by Keuper marl, in which rocks numerous branches of the deposit are met with. After giving a geological sketch of the vicinity of Badenweiler, the author gives the results of his petrographical and chemical investigations of the crystalline rocks of the district. The somewhat coarse-grained granite of the Forstgärtchen contains oligoclase, orthoclase, and mica, analyses of which minerals are given. As further macroscopic constituents, quartz, hornblende, and orthite are met with, whilst magnetite, apatite, zircon, rutile, anatase, and epidote occur microscopically. The minerals found in the ore deposit include barytes (analysis given), quartz, fluorspar, brown-spar, zinc-blende, zinc silicate, galena, anglesite, linarite, cerussite, pyromorphite (three analyses given), yellow lead ore, and copper pyrites. From the last-named mineral, copper glance and copper indigo are produced in indistinct pseudomorphs. Other products of decomposition are chrysocolla, malachite, and limonite. The quartz appears to be younger than the barytes and fluorspar, after which it forms pseudomorphs. The memoir concludes with a discussion of the genesis of the ore deposit by lateral secretion. B. H. B.

Mineral Springs in the Admirals-gartenbad, Berlin. By R. FRESENIUS (*J. pr. Chem.* [2], **38**, 236—240).—On 24th January, 1888, the spring delivered 12·8 litres per minute; the temperature of the water was 15·2°, the air temperature being 5°. The water was perfectly clear, but deposited oxide and phosphate of iron on exposure to air; its sp. gr. at 17·5° was 1·021016; no micro-organisms were developed in the bacteriological research. The detailed analysis is as follows, all the carbonates being calculated as normal carbonate:—

	In 1000 parts by weight.
Sodium chloride	26·715139
Potassium chloride	0·139062
Lithium chloride	0·002197
Ammonium chloride	0·018855
Calcium chloride	0·520697
Magnesium chloride	0·644199
Sodium bromide	0·020943
Sodium iodide	0·000598
Calcium sulphate	0·297493
Strontium sulphate	0·037129
Barium sulphate	trace
Magnesium carbonate	0·245551
Ferrous carbonate	0·008097
Manganous carbonate	0·000160
Aluminium phosphate	0·000107
Aluminium silicate ($Al_2O_3,3SiO_2$)	0·002173
Calcium borate	0·005807
Silica	0·013925
	28·672132
Carbonic anhydride combined with the normal carbonates, to form bicarbonates	0·131754
Free carbonic anhydride	0·014010
	28·817896

The author compares this water with other waters as to its contents of sodium, calcium, and magnesium chlorides, sodium bromide, and sodium iodide. A. G. B.

Analysis of Roncegno-water. By M. Gläser and W. Kalmann (*Ber.*, 21, 2879—2881).—The quantity of water flowing from this medicinal spring, which has its source in the Tesobo Mountain, varies during the year. The analysis of a sample taken at the time of greatest flow is given below; one litre at 18° containing—

H_3AsO_4.	$FeSO_4$.	$Fe_2(SO_4)_3$.	$Fe_2(PO_4)_2$.	$Al_2(SO_4)_3$.	$MnSO_4$.
0·1531	0·0072	3·0980	0·0285	1·5572	0·1684

$CoSO_4$.	$NiSO_4$.	$ZnSO_4$.	$CuSO_4$.	$CaSO_4$.	$MgSO_4$.
0·0353	0·0862	0·0121	0·0306	1·9072	0·3657

K_2SO_4.	Na_2SO_4.	$NaCl$.	SiO_2.	Organic matter.
0·0400	0·3009	0·0043	0·1274	0·2280

Total solids, by direct estimation, 8·1440 grams.

A comparison with the analysis previously given (Abstr., 1888, 796) shows that the quantity of arsenic acid has decreased considerably (38·1 mgrm. per litre), whilst the other constituents are present in almost the same quantities as before. F. S. K.

Analyses of the Waters of some American Alkali Lakes. By T. M. Chatard (*Amer. J. Sci.*, **36**, 146—150).—The four analyses given represent the most important alkali lakes so far known. For determining the boric acid, Gooch's method (Abstr., 1887, 299) was found to be the most accurate. Of the four lakes, the most northern is Albert Lake (I), in south-east Oregon. The sample analysed was taken in September, 1887, 1 foot below surface, and 35 feet from the shore; sp. gr. 1·03117 at 19 8°. II. Big Soda Lake, near Ragtown, Churchill Co., Nevada; sample taken in 1881 at the depth of 1 foot; sp. gr., 1·0995 at 19·8°. III. Mono Lake, California, although of a composition favourable to utilisation, is practically inaccessible on account of its great altitude. The sample was taken in 1882 at the depth of 1 foot; sp. gr. 1·045 at 15·5°. IV. Owen's Lake, Inyo Co., California, is 17 miles long and 9 miles wide, its greatest depth being 51 feet. It is estimated to contain 22 million tons of sodium carbonate. The manufacture of soda at this point has been commenced. The sample was taken in September, 1886; sp. gr. 1·062 at 25°.

The analytical results were as follows, *a* being the composition in grams per litre, and *b* that per cent. of solid constituents:—

	I*a*.	I*b*.	II*a*.	II*b*.	III*a*.	III*b*.	IV*a*.	IV*b*.
SiO_2	0·232	0·59	0·304	0·24	0·070	0·12	0·220	0·28
K	0·538	1·37	2·520	1·95	0·961	1·79	1·644	2·13
Na	14·690	37·51	45·840	35·53	19·685	36·81	28·500	36·96
Ca	—	—	—	—	0·020	0·04	0·014	0·02
Mg	—	—	0·270	0·21	0·055	0·10	0·005	—
Fe_2O_3	—	—	—	—	0·003	0·01	0·014	0·02
Al_2O_3	—	—	—	—			0·024	0·03
SO_4	0·706	1·80	12·960	10·05	6·672	12·48	7·505	9·73
B_2O_7	—	—	0·314	0·24	0·160	0·30	0·367	0·49
CO_3	9·486	24·21	20·934	16·23	13·690	25·61	19·398	25·16
Cl	13·462	34·67	45·690	35·41	12·104	22·64	19·344	25·09
H	0·058	0·15	0·181	0·14	0·052	0·10	0·063	0·10
Totals	39·172	100·30*	129·013	100·00	53·472	100·00	77·098	100·01

B. H. B.

Organic Chemistry.

Isoallylene. By G. Gustavson and N. Demjanoff (*J. pr. Chem.* [2], **38**, 201—207).—Isoallylene may be prepared by the action of zinc-dust on an alcoholic solution of dibromopropylene. The latter, best obtained by the action of potassium hydroxide on tribromhydrin, is allowed to drop slowly into the warm mixture of zinc-dust and 80 per cent. alcohol, contained in a flask. The isoallylene evolved is collected over water, in which it is very little soluble. 10 grams of dibromopropylene yield 900 to 1000 c.c. of the gas.

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* 100·00 in the original paper.

Isoallylene is a colourless gas, smelling like normal allylene; it burns with a strongly luminous flame, and gives no precipitate with ammoniacal cuprous chloride or silver nitrate. With aqueous solutions of mercuric chloride or sulphate it gives a white precipitate. The gas from 10 grams of dibromopropylene was absorbed by 35 grams of bromine, the unaltered bromine dissolved in sodium hydroxide solution, and the colourless oil washed with water. It weighed 17 grams, the calculated yield being 18 grams, and had the formula $C_3H_4Br_4$. *Isoallylene tetrabromide* smells of camphor, and has the sp. gr. 2·729 at 0° and 2·658 at 18° (water at $0° = 1$); it solidifies when cooled to $-18°$, and melts below 0°; at the ordinary pressure it distils between 215° and 230° with partial decomposition. Normal allylene tetrabromide has the sp. gr. 2·690 at 0° and 2·652 at 18°, and does not solidify in a freezing mixture. That the two are not identical is conclusively proved by the fact that by the action of zinc-dust isoallylene is liberated from the one, and normal allylene from the other.

On heating sodium with an ethereal solution of isoallylene in a sealed tube at 100°, the sodium is converted into a white powder, which evolves normal allylene when treated with water. Favorsky has shown that this conversion of iso- into normal hydro-carbons by the action of sodium, is characteristic of the homologues of acetylene.

When passed into strong sulphuric acid, isoallylene is absorbed, and on dilution with water and addition of potassium hydroxide, acetone separates; this is a strong argument in favour of isoallylene being *dimethylenemethane*, $CH_2{:}C{:}CH_2$, thus (1) $CH_2{:}C{:}CH_2 + 2H_2SO_4 = CH_3{\cdot}C(HSO_4)_2{\cdot}CH_3$; (2) $CH_3{\cdot}C(HSO_4)_2{\cdot}CH_3 + H_2O = CH_3{\cdot}CO{\cdot}CH_3 + 2H_2SO_4$. If this is the case, the dibromopropylene from which isoallylene is obtained must be $CH_2Br{\cdot}CBr{:}CH_2$, and isoallylene tetrabromide must be $CH_2Br{\cdot}CBr_2{\cdot}CH_2Br$. A. G. B.

Cyanurates. By A. CLAUS and O. PUTENSEN (*J. pr. Chem.* [2], **38**, 208—229).—The amethyst-coloured crystals, obtained when cyanuric acid is mixed with ammoniacal copper sulphate, have the composition $(C_3N_3O_3H_2)_2Cu,2NH_3$. By digesting them with dilute ammonia, violet needles of the composition $(C_3N_3O_3H_2)_2Cu,3NH_3$ are obtained, and if strong ammonia is used a deep blue compound, $(C_3N_3O_3H_2)_2Cu,4NH_3$, is formed; but this last is very unstable, rapidly losing ammonia in the air. When the first of these ammoniacal copper cyanurates is digested with water, a basic copper cyanurate, $C_3N_3O_3(Cu{\cdot}OH)_3 + 3H_2O$, is formed. An acid copper cyanurate of the composition $(C_3N_3O_3H_2)_2Cu,C_3N_3O_3H_3,NH_3 + H_2O$ is formed when copper carbonate is digested with cyanuric acid and ammonia. The salt, $C_3N_3O_3HCu + 3H_2O$, is precipitated when sodium cyanurate is added to copper sulphate; and normal copper cyanurate, $(C_3N_3O_3)_2Cu_3 + H_2O$, crystallises when acid magnesium cyanurate is mixed with copper sulphate. The following cyanurates are also described: Acid magnesium cyanurate, ammoniacal cadmium cyanurate, ammoniacal zinc cyanurate, ammoniacal nickel cyanurate, cyanurates of nickel, cobalt, and manganese; tetramethylammonium cyanurate, and further, cyanurates of quinoline, quinine, cinchonine, strychnine, narcotine, and caffeïne. A. G. B.

Preparation of α-Dibromhydrin. By O. ASCHAN (*Ber.*, **21**, 2890—2892).—α-Dibromhydrin is best prepared as follows:—Phosphorus tribromide (650 grams) is dropped in quantities of from 10 to 20 grams at a time into pure, warm glycerol (500 grams), the whole being well shaken and cooled after each addition of bromide. The operation is at an end in from three to four hours. After keeping for 24 hours, the mixture is heated on the water-bath for about three hours, cooled, diluted with water (3 to 4 vols.), extracted with ether, and the extract washed with sodium carbonate solution and dried. After evaporating the ether, the residual oil is heated at about 200°, and then fractionated; the portion boiling at 208—218°, which constitutes about two-thirds of the whole, is finally distilled under reduced pressure. 500 grams of glycerol yield 135 grams of pure α-dibromhydrin. The requisite quantities of yellow phosphorus and bromine can be employed instead of phosphorus tribromide.

When α-dibromhydrin is treated with nitric acid of sp. gr. 1·48, the principal product is a liquid boiling at 78—79° (18 mm.), which contains bromine and nitrogen. It forms very stable, yellow, readily crystallisable salts. F. S. K.

Epichlorhydrin. By C. PAAL (*Ber.*, **21**, 2971—2973).—*Chloriodohydrin methyl ether*, $C_3H_5ClI·OMe$, is obtained by heating epichlorhydrin (1 mol.) with methyl iodide (1 mol.) at 190°, fractionating the product, and removing the free iodine with finely divided silver. The yield is about 20 per cent. of the theoretical quantity. It is a colourless oil with a pungent smell, exceedingly sensitive to light, and miscible with the ordinary solvents excepting water, in which it is insoluble. It boils at about 200° with partial decomposition, and is readily volatile with steam.

Chloriodohydrin ethyl ether, $C_3H_5ClI·OEt$, is prepared by heating epichlorhydrin with ethyl iodide at 200—220°, and purifying the product as described above. The yield is 30—50 per cent. of the theoretical quantity. It boils at 200—210° with slight decomposition and resembles the preceding compound.

Chloriodohydrin isopropyl ether, $C_3H_5ClI·OPr^{\beta}$, prepared in like manner, boils at 208—212° with partial decomposition and resembles the ethyl ether. The *normal propyl ether* boils at 200—210° with slight decomposition; it is relatively stable and less sensitive to light than the other ethers which, however, it resembles in other respects.

F. S. K.

Propyl-phycite. By A. FAUCONNIER (*Compt. rend.*, **107**, 629—630). —The action of hypochlorous acid on epichlorhydrin results in the assimilation of water, most probably because of the acidity of the liquid, and the "propyl-phycite" obtained by Carius by saponifying the product of this reaction, and described by him as a lower homologue of erythrol, is in reality ordinary glycerol. C. H. B.

Molecular Weight and Valency of Perseite. By MAQUENNE (*Compt. rend.*, **107**, 583—586).—When perseite is treated with boiling hydriodic acid, it is partly converted into resinous products of indefinite composition, and partly into a volatile liquid which can be separated into two fractions boiling at 100—110° and 190—200° respectively. The first is a heptine, isomeric with œnanthylidene, which boils at 102—105° after rectification over calcium oxide and over sodium; sp. gr. at 20° = 0·78. The second fraction is a dense red oil with a slight ethereal odour. It boils at 192—196° under ordinary pressure, and at 92—95° under a pressure of 40—50 mm., but decomposes to a considerable extent even when distilled in a vacuum. It consists mainly of heptyl iodide with a small quantity of heptine hydriodide.

The *dibenzoic acetal of perseite*, $C_{21}H_{24}O_7$, is obtained by the action of benzaldehyde on perseite in presence of alcohol saturated with hydrogen chloride. It forms confused, slender, microscopic needles which soften at 215°, but have no definite melting point, and are quite insoluble in water and almost insoluble in alcohol.

These results show that the formula previously attributed to perseite (Abstr., 1888, 807) is incorrect, and that perseite is really the next higher homologue of mannitol, and has the formula $C_7H_{16}O_7$. It is the first instance of a heptahydric alcohol and of a sugar containing 7 carbon-atoms. C. H. B.

Constitution of the Glucoses. By B. RAÝMANN (*Ber.*, **21**, 2841—2842).—The author considers that the aldehyde and ketone formulæ explain the chief reactions of the glucoses, and that the reactions which Tollens mentions (*Kurzes Handb. d. Kohlenhydrate*), as incompatible with the assumption that these compounds are aldehydes do not afford sufficient grounds for changing the formulæ.

N. H. M.

Oxidation of Arabinose with Nitric Acid. By H. KILIANI (*Ber.*, **21**, 3006—3009).—Calcium arabonate is obtained in considerable quantities when arabinose (1 part) is heated at 35° for about six hours with nitric acid of sp. gr. 1·2 (2 parts), the diluted solution boiled with excess of calcium carbonate, filtered, evaporated, and mixed with alcohol. This method can be suitably employed for the preparation of arabonic acid.

Calcium trihydroxyglutarate is obtained from arabinose as follows:—Arabinose (1 part) is digested at 35° with nitric acid of sp. gr. 1·2 (2·5 parts); after the evolution of gas has ceased, the solution is evaporated until free from nitric acid, the residual syrup dissolved in water (25 parts), boiled with calcium carbonate, and the hot solution filtered. The sparingly soluble, red calcium salt which separates is spread on porous plates, and by concentrating the mother-liquor, separating the salt, and repeating the process several times, 40—45 per cent. of the weight of the arabinose employed is obtained in the form of calcium trihydroxyglutarate. It is very similar to calcium saccharate in appearance and in its behaviour when heated with water. The *potassium* salt, $C_5H_6O_7K_2$, crystallises in large, colourless, monoclinic plates or prisms, is readily soluble, and is not converted into the acid salt when the aqueous solution is evaporated with acetic acid. Lead acetate and silver nitrate produce white precipitates in an aqueous solution.

Trihydroxyglutaric acid, $C_5H_8O_7$, obtained by decomposing the calcium salt with oxalic acid, crystallises from alcohol in colourless, microscopic plates, melts at 127°, and does not reduce Fehling's solution. The normal ammonium salt crystallises in slender needles and is very readily soluble. F. S. K.

Action of Nitrous Acid on Hexamethyleneamine. By F. MAYER (*Ber.*, 21, 2883—2890).—*Trimethylenetrinitrosamine*, $C_3H_6N_6O_3$, is obtained when an ice-cold solution of hexamethyleneamine (1 part) in water (40 parts) is mixed with ice-cold, dilute ($1\frac{1}{2}$ per cent.) hydrochloric acid, and a solution of sodium nitrite ($2\frac{1}{2}$ parts) in a small quantity of water immediately added. After about 15 minutes, the yellowish, crystalline substance which separates at the surface is thrown on to a filter, washed with cold water, and dried on porous plates. The yield is 50 to 60 per cent., or more, of the amine employed. It crystallises from boiling alcohol, in which it is moderately soluble, in small, yellowish, silky needles or prisms, melts at 105—106°, and is readily soluble in cold acetone, but only moderately so in warm benzene, chloroform, and ether, and insoluble in light petroleum. It dissolves unchanged in cold glacial acetic acid, and the molecular weight determined by Raoult's method was found to be 196. On exposure to moist air, the crystals lose their silky appearance, and when treated with cold water, a slight evolution of nitrogen occurs. It melts under boiling water to a yellowish oil which gradually dissolves with evolution of nitrogen, and the solution contains formaldehyde. The same decomposition takes place, but much more quickly, when it is warmed with glacial acetic acid or dilute acids, but the decomposition into formaldehyde and nitrogen is not quite quantitative, as traces of ammonia are formed at the same time. When heated in a capillary tube, or when treated with concentrated acids, it is immediately decomposed with evolution of nitrous fumes, and when heated on platinum foil it explodes. It gives Liebermann's reaction. The filtrate obtained in the preparation of this compound contains unchanged hexamethyleneamine; if, however, the mixture is kept for a long time before separating the nitrosoamine, the latter is decomposed into formaldehyde and nitrogen, and some of the hexamethyleneamine is converted into formaldehyde and ammonia.

Dinitrosopentamethylenetetramine was obtained by gradually adding dilute hydrochloric acid to a solution of hexamethyleneamine and sodium nitrite (compare Griess and Harrow, Abstr., 1888, 1268). It melts at 202—203°, and gives Liebermann's nitroso-reaction.

F. S. K.

Identity of Putresine and Tetramethylenediamine. By L. v. UDRÁNSZKY and E. BAUMANN (*Ber.*, 21, 2938—2941).—A direct comparison of the dibenzoyl-derivatives of putresine (Brieger), tetramethylenediamine, and the compound obtained by the authors from the urine of a patient suffering from cystinuria (compare Abstr., 1888, 1296), proved that these bases are identical.

Concentrated solutions of guanidine, creatine, creatinine, and similar compounds give a precipitate with soda and benzoic chloride, whereas no separation occurs in solutions containing less than 0·5 gram of the bases; it is therefore necessary that when benzoic chloride is used as a reagent for diamines (*loc. cit.*) only very dilute solutions of the latter should be employed. F. S. K.

Decomposition of Acetone with Bleaching Powder. By W. R. ORNDORFF and H. JESSEL (*Amer. Chem. J.*, **10**, 363—367).—Liebig stated that acetone could advantageously be substituted for alcohol in the preparation of chloroform; this statement has been contradicted by Siemerling, yet chloroform is now largely made from acetone. In a number of trials, the yield was 166 to 173 per cent. of the weight of the acetone used, and the residual liquors contained considerable quantities of calcium acetate. The reaction is represented by $2CO(CH_3)_2 + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + Ca(CH_3{\cdot}COO)_2$. Liebig states that calcium carbonate is precipitated during the reaction, but the precipitate is calcium hydroxide. Acetophenone similarly treated with bleaching powder, yields chloroform, calcium hydrate, and calcium benzoate. H. B.

Dinitrosoacetone. By H. v. PECHMANN and K. WEHSARG (*Ber.*, **21**, 2989—2993).—When dinitrosoacetone (compare Abstr., 1887, 28) is boiled with water or acids, it is decomposed into carbonic anhydride, hydrogen cyanide, water, and ammonium hydrogen oxalate; but when it is heated with glacial acetic acid, oxamic acid, melting at 210°, and hydrogen cyanide are formed.

Trinitrosopropane, $NOH{:}CH{\cdot}C(NOH){\cdot}CH{:}NOH$, prepared by heating a mixture of dinitrosoacetone (1 mol.), hydroxylamine hydrochloride (1 mol.), sodium acetate (1 mol.), and water at 50—60° for 1 to 2 hours, separates from hot water in the form of a colourless, crystalline powder melting at 171° with sudden decomposition. It is only sparingly soluble in ether, but readily soluble in alcohol, from which it crystallises in needles, and it dissolves slowly, but in considerable quantities, in hot water. It behaves like dinitrosoacetone when heated with dilute acids, but its aqueous solution can be boiled for a short time without decomposition taking place. Ferric chloride gives a brownish-red coloration with a dilute aqueous solution; ferrous sulphate produces a wine-red colour, and the solution then gives a violet precipitate with soda.

Dinitrosoacetonehydrazone, $NOH{:}CH{\cdot}C(N_2HPh){\cdot}CH{:}NOH$, prepared by treating dinitrosoacetone (1 mol.) with phenylhydrazine (1 mol.) in hot, alcoholic solution, crystallises in yellow needles, melts at 145° with decomposition, and is readily soluble in alcohol and ether, more sparingly in benzene and light petroleum, and insoluble in water. It dissolves in alkalis with a yellow, and in concentrated sulphuric acid with an orange-yellow coloration. The *acetyl*-derivative, $C_9H_9N_4O_2Ac$, a light yellow, crystalline compound, melts at 133°, and is soluble in dilute alcohol. It dissolves in alkalis with a yellowish coloration, but the solution becomes colourless on boiling, and on adding acids, a compound, $C_9H_8N_4O$, is precipitated in shining, colourless needles. This substance is also formed when the acetyl-derivative is boiled with water. A compound, $C_{15}H_{12}N_4$, is obtained when dinitrosoacetone is heated with excess of phenylhydrazine acetate. It crystallises from hot alcohol or benzene in shining, yellow plates melting at 122°. It is not acted on when boiled with ferric chloride, and its solution in concentrated sulphuric acid does not give a coloration with this reagent. F. S. K.

Sulphoisovaleric Acid. By G. de Varda (*Chem. Centr.*, 1888, 887—888, from *Rend. Acad. dei Lincei* [4], **4**, 1).—100 parts of isovaleric acid are mixed with 100 parts of chlorosulphonic acid, and, after the spontaneous reaction has ended, the mass is heated to 150°; it is then diluted with several volumes of water, and distilled from the oil-bath until the distillate no longer has an acid reaction. The distillate is then heated with plumbic carbonate for some time, filtered while hot, and the lead precipitated from the solution by hydrogen sulphide, the solution of the free acid being concentrated in a vacuum.

Sulphoisovaleric acid so obtained forms deliquescent crystals. The aqueous solution partly decomposes when heated on the water-bath. The lead salt, $C_5H_8SO_5Pb.2H_2O$, crystallises from water in colourless, odourless, small plates, which taste sweet; they are slightly soluble in water, and insoluble in alcohol, ether, and chloroform. The barium salt, containing 1 mol. H_2O, forms small, tabular crystals, without smell or colour, and taste bitter. It is soluble in water, insoluble in alcohol, ether, and chloroform. J. W. L.

Constituents of Cocoa Fat. By P. Graf (*Arch. Pharm.* [3], **26**, 830—846; comp. Kingzett, Trans., 1878, 38).—The melting point of various samples of commercial cocoa butter from widely different sources was determined both in open and closed glass tubes. In the open tube, the results varied from 29° to 33·4°, whilst in the closed tube 11 samples gave 34·3° and one 33·5°. The whole of the samples were mixed together for the further investigation. The fat was found to contain hardly any free acid. Two determinations of glycerol averaged 9·59 per cent. A little cholesterin and small quantities of formic, acetic, and butyric acids were detected. After the separation of oleic acid, the solid fatty acids were isolated by fractional crystallisation, followed by Heintz's method of fractional precipitation by means of magnesium and barium acetates. No acid with a higher molecular weight than arachidic acid was found; this confirms Traub's statement that he was unable to find theobromic acid asserted to be present by Kingzett. The presence of oleic, stearic, and palmitic acids was confirmed; and either lauric acid or one of its isomerides was isolated: there was not sufficient material at hand to settle this point. J. T.

Action of Hydrogen Phosphide on Aldehydes and Ketone Acids. By J. Messinger and C. Engels (*Ber.*, **21**, 2919—2928).—The compound obtained by passing hydrogen phosphide and hydrogen chloride into an ethereal solution of pyruvic acid has the constitution $P(CMe<{}^{O}_{CO}>)_3$, and is named by the authors *phosphorus-trianhydropyruvic acid* (compare Abstr., 1888, 441). It is insoluble in cold acids, and on heating, decomposition takes place. It dissolves in warm, glacial acetic acid, and separates unchanged on cooling. It is not acted on by bromine even at 150°, but when boiled with water it is decomposed into pyruvic acid and hydrogen phosphide.

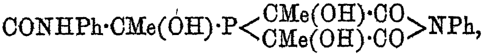
Phosphorus-trihydropyruvic acid hydrazide,

$$P[CMe(OH)\cdot C(OH):N_2HPh]_3,$$

is formed when the preceding compound is warmed with phenylhydrazine in alcoholic solution; it is a colourless, crystalline compound, melts at 132°, and is moderately soluble in alcoholic ether, but only sparingly in cold alcohol, and almost insoluble in ether.

Hydrazonepyruvic acid hydrazide, $C_{15}H_{16}N_4O$, is formed, together with hydrogen phosphide, when phosphorustrianhydropyruvic acid is heated with excess of phenylhydrazine, in which it is readily soluble. It crystallises from hot alcohol in colourless, shining plates, melts at 162°, and is only sparingly soluble in cold alcohol and ether.

Phosphorus-trihydropyruvic acid dianilide,



$$CONHPh\cdot CMe(OH)\cdot P<{}^{CMe(OH)\cdot CO}_{CMe(OH)\cdot CO}>NPh,$$

is obtained when aniline is gradually added to an alcoholic solution of phosphorus-trianhydropyruvic acid. It separates from warm alcohol in colourless crystals, melts at 158°, is very sparingly soluble in cold alcohol and insoluble in water or ether. It is completely decomposed, with separation of phosphorus, when treated with hydrogen chloride in alcoholic or ethereal solution.

Dihydrazonepyruvic acid hydrazide, $NPh(CO\cdot CMe:N_2HPh)_2$, is formed when the preceding compound is treated with phenylhydrazide. It crystallises from alcohol in small needles melting at 169°.

Phosphorus-trianhydropyruvic acid and toluylenediamine yield a crystalline compound, $C_9H_9O_6P + 2C_6H_3Me(NH_2)_2$, which melts at 178° with decomposition.

Hydrogen phosphide, in presence of hydrogen chloride, has no action on ethyl acetoacetate or benzoylcarboxylic acid, but tribromopyruvic acid absorbs the gas in considerable quantities with evolution of hydrogen bromide and the ultimate formation of phosphorus-trianhydropyruvic acid. F. S. K.

Action of Heat on Tartaric Acid in Aqueous Solution. By E. M. WEDARD (*Chem. Centr.*, 1888, 889, from *Atti. R. Acad. Sci. Torino*, **6**, 65—67).—The author noticed that when tartaric acid had been heated for several days in sealed tubes with ferrous sulphate, several of the tubes exploded violently, and in the others a considerable quantity of carbonic anhydride was found. As the ferrous salt had not become oxidised at all, the reaction had not been a simple reduction of the tartaric acid. Tartaric acid heated with water alone at 150° in sealed tubes also suffered a considerable loss of carbonic anhydride. In one experiment, the author opened the tube after heating, allowed the carbonic anhydride to escape, then sealed it again, and submitted the contents to a further heating, and repeated the operation until no further evolution of carbonic anhydride took place, after which the resulting liquid was found to contain pyrotartaric acid along with undecomposed tartaric acid. J. W. L.

Freezing Points of Solutions of Aluminium Alkyls. By E. Louise and L. Roux (*Compt. rend.*, **107**, 600—603).—Pure ethylene bromide was used as a solvent, the molecular reduction, T, with this liquid being 118. The number obtained with mercury propyl was 124·8; mercury isobutyl, 122·7; mercury isoamyl, 123·6; mercury phenyl, 120·4.

Aluminium ethyl gave a molecular reduction of 115·6, which agrees with the formula Al_2Et_6.

Aluminium propyl, obtained by the action of aluminium on mercury propyl, is a colourless, mobile liquid, which boils at 250° and takes fire in contact with the air. *Aluminium isoamyl*, obtained in a similar way, is a somewhat viscous, colourless liquid, with an odour of amyl compounds; it boils at 250° under a pressure of 80—100 mm., and does not readily take fire in contact with the air. The molecular reduction with aluminium propyl is 92·8, and with aluminium isoamyl 84·5. These values agree more closely with the formula Al_2R_6 than with AlR_3, and hence confirm the conclusions deduced from vapour-density determinations (Abstracts, 1888, 583).

C. H. B.

Substituted Pyromucic Acids. By H. B. Hill and A. W. Palmer (*Amer. Chem. J.*, **10**, 373—391).—With the exception of a sulphopyromucic acid briefly described by Schwanert, no furfuran-derivatives containing the sulphonic group are described; yet the general behaviour of pyromucic acid is similar to that of benzoic acid.

δ-Sulphopyromucic acid is readily formed by treating pyromucic acid with fuming sulphuric acid. The acid itself is extremely soluble in water, but may be obtained in large, deliquescent crystals. The following salts are described: $BaC_5H_2SO_6 + 4H_2O$; $Ba(C_5H_3SO_6)_2 + 4H_2O$, and also with $6H_2O$; $CaC_5H_2SO_6 + 3H_2O$; $PbC_5H_2SO_6 + 2H_2O$, all readily soluble in hot water; $Ag_2C_5H_2SO_6$ is sparingly soluble in water; $K_2C_5H_2SO_6 + 4H_2O$; $KC_5H_3SO_6$; $Na_2C_5H_2SO_6 + 5H_2O$, and $NaC_5H_3SO_6 + H_2O$, all very soluble. All these salts crystallise readily. By treating the dry sodium salt with phosphorus pentachloride, and the resulting viscous oil with ammonia, the crystalline *δ-sulphopyromucamide*, $C_5H_2SO_4(NH_2)_2$, is obtained; it is readily soluble in hot water, and melts at 213°. The dry acid is only decomposed by bromine at 100°, dibromosuccinic acid and other products being formed; in aqueous solution the acid is mainly converted into fumaric acid. Dilute nitric acid oxidises it slowly, and also produces fumaric acid and some oxalic acid; concentrated nitric acid at 100° readily converts it into Klinkhardt's δ-nitropyromucic acid, and at the same time a neutral substance, in all probability αα-dinitrofurfuran, is formed.

Although bromine-derivatives of δ-sulphopyromucic acid cannot be obtained by the action of bromine, they may be obtained by sulphonating the corresponding bromopyromucic acids: *β-Bromo-δ-sulphopyromucic acid* is extremely soluble in cold water, and forms deliquescent crystals. The salts—

$$BaC_5HBrSO_6 + 4H_2O;\ CaC_5HBrSO_6 + 6H_2O;\ PbC_5HBrSO_6 + 4H_2O;$$
$$K_2C_5HBrSO_6 + 1\tfrac{1}{2}H_2O\ (?)$$

are described; they are all crystalline and soluble in water. That the acid is really a derivative of δ-sulphopyromucic acid is proved by obtaining this acid by treatment of the bromo-acid with zinc and ammonia. Bromine in aqueous solution readily converts the bromo-acid into monobromofumaric acid. Concentrated nitric acid readily yields *β-bromo-δ-nitropyromucic acid*, soluble in water, alcohol, &c., and melting at 159—160°.

β-γ-Dibromo-δ-sulphopyromucic acid is prepared by dissolving β-γ-dibromopyromucic acid in fuming sulphuric acid, but it is more advantageous to use the mixture of β-γ- and β-δ-dibromopyromucic acids resulting from the decomposition of the tetrabromo-acid, as the β-δ-dibromo-acid is but little acted on by the sulphuric acid. The acid in question is very soluble in water, and is crystalline; the following salts are described: $BaC_5Br_2SO_6 + 5H_2O$ and also with $3H_2O$; $PbC_5Br_2SO_6 + 4H_2O$; $Ag_2C_5Br_2SO_6 + H_2O$; $K_2C_5Br_2SO_6 + H_2O$. That the sulphonic acid occupies the δ-position, the only possible one, is proved by treatment of the above barium salt with zinc-dust and ammonia, when the δ-sulphopyromucic acid first described is obtained. Bromine in aqueous solution readily oxidises the barium salt, giving barium sulphate and dibromomaleic acid. Dilute nitric acid oxidises it to dibromosuccinic acid. Concentrated nitric acid yields a mixture of β-γ-dibromo-δ-nitropyromucic acid, crystallising from water in sparingly soluble, slender, yellow needles, that melt at 204—205°, and ββ-dibromo-αα-dinitrofurfuran, a substance melting at 150—151° and crystallising from benzene, as the compound $C_4Br_2(NO_2)_2O,C_6H_6$, which readily gives off this benzene of crystallisation. H. B.

Metadiethylbenzene. By A. Voswinkel (*Ber.*, **21**, 2829—2831). *Metadiethylbenzene*, $C_6H_4Et_2$, is obtained, together with the para-compound, by the action of ethyl bromide and aluminium chloride on benzene; the two compounds are separated from each other by means of the barium sulphonates. It boils at 181—182°, and does not solidify at −20°, but becomes thicker. Sp. gr. = 0·8602 at 20° compared with water at 4°. When boiled with dilute nitric acid, ethylbenzoic and isophthalic acids are formed. The *barium sulphonate* (with 3 mols. H_2O) crystallises in hemispherical groups of prisms, rather sparingly soluble in cold water. The *copper salt* (with 4 mols. H_2O) forms bright-blue plates of a satiny lustre; the *potassium salt* (with 1 mol. H_2O) crystallises in quadratic plates. The *sulphonamide* separates from the dilute alcoholic solution in long, flat needles, melting at 101—102°. The *bromine-derivative*, $C_6H_3Et_2Br$, boils at about 238°. The *tetrabromo-compound*, $C_6Et_2Br_4$, crystallises from alcohol in small, colourless prisms melting at 74°. *Nitrometadiethylbenzene*, $C_6H_3Et_2{\cdot}NO_2$, is a pale yellow liquid, which boils at

280—285°, with decomposition. The *trinitro-compound*, $C_6HEt_2(NO_2)_3$, crystallises from light petroleum in prisms melting at 62°. *Amidometadiethylbenzene*, $C_6H_3Et_2·NH_2$, prepared by reducing the nitro-derivative, is a colourless liquid which distils readily with steam; the *hydrochloride* crystallises in groups of very long needles; the *acetyl-derivative* forms stellate groups of needles melting at 104°. *Metadiethylphenol*, $C_6H_3Et_2·OH$, is obtained by fusing the sulphonic acid with potash; it boils at 225°, and dissolves sparingly in water; the solution gives a blue-violet colour (which changes to green on adding alcohol) with ferric chloride. *Meta-ethylbenzoic acid*, $C_6H_4Et·COOH$, crystallises in long needles, melts at 47°, and is almost insoluble in water. The *calcium salt* (with 4 mols. H_2O) forms lustrous needles, readily soluble in water and alcohol. N. H. M.

Synthesis of Consecutive Tetramethylbenzene. By O. JACOBSEN (*Ber.*, **21**, 2821—2828).—*Dinitrobromopseudocumene*,

$$[(NO_2)_2 : Br : Me_3 = 5 : 6 : 2 : 1 : 3 : 4],$$

obtained by the action of nitric and sulphuric acids on bromopseudocumene [$Br : Me_3 = 2 : 1 : 3 : 4$], crystallises from hot alcohol in small, yellowish-white, lustrous prisms, melts at 182°, and dissolves readily in hot benzene, sparingly in hot alcohol.

Bromopseudocumene, [$Br : Me_3 = 2 : 1 : 3 : 4$], has the same boiling point as the 5, 1, 3, 4 compound: 237—238° (not 226—229°). The sulphonamide melts at 185° (not 187—188°; compare Kelbe and Pathe, *Ber.*, **19**, 1546).

1, 2, 3, 4-Tetramethylbenzene is prepared by heating pure bromopseudocumene (25 grams), methyl iodide (40 grams), and sodium (14 grams), in presence of sufficient absolute ether to cover the latter. After two or three days, it is distilled. The yield of tetramethylbenzene is 38 per cent. of the weight of the bromopseudocumene.

Dibromometaxylene, [$Me_2 : Br_2 = 1 : 3 : 2 : 4$], is obtained in the preparation of symmetrical dibromometaxylene by brominating the hydrocarbon; it is an oily liquid which, when cooled, solidifies to a hard crystalline mass melting at −8°, and boils at 269° under 760 mm. pressure. The *dinitro-derivative* forms almost colourless, microscopic crystals, melts at 191°, and dissolves readily in toluene, very sparingly in alcohol. When exposed to light it becomes yellow. The *sodium sulphonate*, $C_6HMe_2Br_2·SO_3Na + H_2O$ [$= 1 : 3 : 2 : 4 : 6$], crystallises in groups of needles; the *potassium salt* with 1 mol. H_2O forms lustrous plates, sparingly soluble in cold water; the *barium salt* crystallises in small prisms. The *amide* separates from alcohol in small prisms, which melt with decomposition above 300°. When the sodium salt is treated with zinc-dust and ammonia, the salt of ordinary unsymmetrical metaxylenesulphonic acid is formed.

Orthodiamidometaxylene, [$Me_2 : (NH_2)_2 = 1 : 3 : 5 : 6$], is obtained by very prolonged action of tin and hydrochloric acid on the dinitrodibromo-compound, and is liberated from its hydrochloride by dry distillation with sodium carbonate in a stream of hydrogen. It crystallises from water in rhombic plates, melts at 78·5°, and dissolves readily in alcohol, ether, and hot water. When exposed to moist air, it becomes grey-violet. The constitution of this compound as given is proved by the synthesis of 1, 2, 3, 4-tetramethylbenzene from the liquid dibromometaxylene by the action of methyl iodide and sodium, using ether as a diluent.

When symmetrical dibromometaxylene is heated with sulphuric acid (3 parts) at 240°, it is converted into the liquid isomeride.

N. H. M.

Tetrethylbenzene. By O. JACOBSEN (*Ber.*, **21**, 2819—2821).—*Symmetrical tetrethylbenzene*, $C_6H_2Et_4$ [$Et_4 = 1 : 2 : 4 : 5$], is obtained, together with a smaller amount of the isomeride [$Et_4 = 1 : 2 : 3 : 4$], by the action of ethyl bromide on benzene in presence of aluminium chloride, at a temperature not above the boiling point of the bromide; the product is sulphonated in the cold and the sodium sulphonate heated at 170° with hydrochloric acid. It melts at 13°, and boils at 250°. When boiled with dilute nitric acid, and the product further oxidised with permanganate, pyromellitic acid is formed.

Dibromotetrethylbenzene, $C_6Br_2Et_4$ [$Et_4 = 1 : 2 : 4 : 5$], crystallises from hot alcohol in long, thin prisms melting at 112·5°.

Sodium tetrethylbenzenesulphonate, $C_6H\ Et_4\cdot SO_3Na + 4H_2O$, crystallises from water in very large, lustrous plates, sparingly soluble in cold water, much more readily in alcohol, almost insoluble in cold dilute aqueous soda. The *barium salt* (with 9 mols. H_2O) is sparingly soluble in hot water. The *sulphonamide*, $C_{14}H_{21}\cdot SO_2\cdot NH_2$, crystallises from hot dilute alcohol in rhombic plates, melting at 122°.

N. H. M.

Pentethylbenzene and its Decomposition by Sulphuric Acid. By O. JACOBSEN (*Ber.*, **21**, 2814—2819; compare Abstr., 1887, 660; 1888, 137).—*Pentethylbenzene*, C_6HEt_5, is prepared by the action of ethyl bromide on benzene in presence of aluminium chloride, and purified in a manner similar to the pentamethyl-compound (*loc. cit.*). It forms a thick oil, which boils at 277°, and does not solidify at −20°. Sp. gr. = 0·8985 at 19°.

Bromopentethylbenzene, C_6BrEt_5, obtained by brominating the hydrocarbon dissolved in glacial acetic acid, crystallises from alcohol in long needles, melts at 47·5°, and boils at about 315°. It is readily soluble in hot alcohol.

The *sulphone*, $SO_2(C_6Et_5)_2$, crystallises from light petroleum containing some alcohol in large, transparent, hexagonal prisms of a glassy lustre, melts at 76°, and is very readily soluble in alcohol, much less in light petroleum, and insoluble in water.

Sodium pentethylbenzenesulphonate, $C_{16}H_{25}\cdot SO_3Na + 4H_2O$, crystallises from water in thin, lustrous plates, moderately soluble in hot water, much more soluble in alcohol. The anhydrous salt crystallises from 90 per cent. alcohol in groups of hair-like needles. The *potassium salt* (with 2 mols. H_2O) crystallises in thin plates, rather readily soluble in hot water, much more soluble in alcohol. The *ammonium* (with 1 mol. H_2O) and *barium* (with 9 mols. H_2O) *salts* crystallise respectively in large, thin plates and small scales. When pentethylbenzene is treated with an equal volume of sulphuric acid so much fuming sulphuric acid added to the cooled mixture that a clear, brownish-yellow solution is obtained, and the whole kept for 4—5 days at the ordinary temperature, hexethylbenzene and tetrethylbenzene [Et_4 = 1 : 2 : 3 : 4] are formed.

Hexethylbenzene melts at 129° and boils at 298°.

Tetrethylbenzene [Et_4 = 1 : 2 : 3 : 4] boils at 254°, and does not solidify at −20°. It is probably identical with Galle's compound (Abstr., 1883, 1091). The *dibromo-derivative*, $C_6Br_2Et_4$, crystallises in prisms of a glassy lustre, melts at 77°, and is sparingly soluble in boiling alcohol.

Barium tetrethylbenzenesulphonate, $(C_{14}H_{21}\cdot SO_3)_2Ba + 6H_2O$, crystallises from water in flat prisms of a glassy lustre; the *sodium salt* (with 5 mols. H_2O) forms readily soluble. rhombic plates. The *amide* separates from its solution in water and alcohol in well-formed crystals of a glassy lustre, and melts at 107°. N. H. M.

Synthesis of Aromatic Selenium Compounds. By C. CHABRIÉ (*Bull. Soc. Chim.*, **50**, 133—137).—*Phenyl selenide*, $SePh_2$, is obtained by adding aluminium chloride to selenium tetrachloride (1 part) and benzene (3 parts), contained in a reflux apparatus, until no more hydrogen chloride is evolved. The temperature in the flask varies from 22° to 27°, and the operation is finished in about 60 hours. It boils at 227° under a few cm. pressure. Phenyl chloride and an oil boiling at 250° under a pressure of a few cm. are also formed.

Selenium oxychloride in presence of aluminium chloride and selenious anhydride, also react with benzene. N. H. M.

Consecutive Metaxylenol. By O. JACOBSEN (*Ber.*, **21**, 2828—2829).—The author previously (Abstr., 1878, 412) ascribed to consecutive metaxylenol the melting point 74·5°. Nölting isolated the compound from commercial xylidine, and found the melting point 49°. This melting point is now confirmed by preparing metaxylenol by heating pure parahydroxymesitylic acid; the product melted at 47—48°. The xylenol previously obtained (*loc. cit.*) was paraxylenol. N. H. M.

Nitronitrosoresorcinol. By C. DE LA HARPE and F. REVERDIN (*Bull. Soc. Chim.*, **49**, 760—763).—*Nitronitrosoresorcinol*,

$$[OH : NO_2 : O : NOH = 1 : 2 : 3 : 4],$$

is obtained when a cooled mixture of nitroresorcinol (1 mol.), melting at 85°, with a solution of soda (1 mol.) in 10 parts of water and an aqueous solution of sodium nitrite (1 or 2 mols.) is gradually added to excess of dilute and well-cooled sulphuric acid. The yellow, flocculent precipitate is washed with water, dried over sulphuric acid, and extracted with ether to remove traces of nitrosoresorcinol. It crystallises from alcohol in brownish needles, and is readily soluble in water, acids, and alkalis, but only moderately soluble in alcohol, and insoluble in ether, benzene, and chloroform. It is not changed when heated to about 200°, but at higher temperatures it deflagrates violently. It yields diamidoresorcinol (compare Fitz, *Ber.*, **8**, 631) when reduced with tin and hydrochloric acid. The aqueous solution gives an intense green coloration with ferrous sulphate or with iron filings, and a slightly acid solution of the colouring matter, which can-be precipitated from the aqueous solution by adding sodium chloride, dyes wool green (compare Fèvre, Abstr., 1883, 733). Concentrated sulphuric acid added to a mixture of resorcinol and nitronitrosoresorcinol, produces a green colour, which changes to blue and then to a dirty violet; from this solution water precipitates brown flocks, which dissolve in alkalis with a greenish-brown coloration.

Nitroresorcinol, $[(OH)_2 : NO_2 = 1 : 3 : 4]$, melting at 115°, does not form a nitroso-derivative when treated as described above.

F. S. K.

Condensation-product of Quinone and Ethyl Acetoacetate. By H. v. PECHMANN (*Ber.*, 21, 3005—3006).—A condensation-product, $C_{16}H_{16}O_6$, is formed when quinone (1 gram) is heated at 100° with ethyl acetoacetate (2·5 grams) and a 50 per cent. solution of zinc chloride (6 grams) in absolute alcohol. It melts at 184°, and is soluble in boiling alcohol or glacial acetic acid, but insoluble in water. The solution in concentrated sulphuric acid turns deep blue when heated. It yields crystalline derivatives when treated with bromine, but it is not acted on by phenylhydrazine, benzoic chloride, sodium ethoxide and alkyl iodides, or by boiling hydriodic acid. A crystalline bibasic acid, $C_{14}H_{12}O_6$, is precipitated when the preceding compound is hydrolysed with alcoholic potash and the solution acidified with acetic acid. It sublimes without melting, and is insoluble in all ordinary solvents. The *potassium* salt, $C_{14}H_{10}K_2O_6 + 2H_2O$, is a colourless, crystalline, sparingly soluble compound, and loses its water at 125°.

F. S. K.

Derivatives of Paramidoisobutylbenzene. By C. GELZER (*Ber.*, 21, 2941—2949, and 2949—2961).—*Paracetamidobromisobutylbenzene*, $C_4H_9·C_6H_3Br·NHAc$, prepared by brominating acetamidoisobutylbenzene, crystallises from hot dilute alcohol or benzene in large, shining scales or plates, and melts at 153°. It is readily soluble in alcohol, hot benzene, ether, carbon bisulphide, and chloroform, but only very sparingly soluble in boiling water.

Amidobromisobutylbenzene, $C_4H_9·C_6H_3Br·NH_2$, is a heavy, yellowish, aromatic-smelling oil, boiling at 264—265° (710 mm.) with decomposition, and volatile with steam; it is readily soluble in alcohol, ether, and benzene, but insoluble in water. The *hydrochloride*, $C_{10}H_{14}NBr,HCl$, crystallises from benzene in moss-like needles, and is readily soluble in water, alcohol, and warm benzene, but almost insoluble in ether. The *platinochloride*, $(C_{10}H_{14}NBr)_2,H_2PtCl_6$, obtained by precipitating a cold alcoholic solution of the base with a hydrochloric acid solution of platinic chloride, crystallises in slender, yellow needles, and is readily soluble in alcohol, but only sparingly in cold water, and insoluble in ether; it is decomposed when boiled with water. A light yellow, crystalline substance, $(C_{10}H_{14}NBr)_2PtCl_8$, is obtained when a cold alcoholic solution of the base is precipitated with a neutral solution of platinic chloride; it is sparingly soluble in cold alcohol, and is decomposed when the solution is heated. The *picrate*, $C_{10}H_{14}NBr,C_6H_3N_3O_7$, separates from a mixture of warm benzene and light petroleum in slender, yellow, spear-shaped crystals, and is readily soluble in cold alcohol, ether, or hot water, but only sparingly in cold water or cold benzene, and moderately soluble in hot benzene.

Bromisobutylbenzene, $C_4H_9{\cdot}C_6H_4Br$, obtained by treating the amido-derivative with nitrous acid and distilling the product, is a heavy, slightly yellow, aromatic-smelling oil, boiling at 231—232° (710 mm.), and only slightly volatile with steam. It is readily soluble in alcohol, ether, and benzene, but insoluble in water. It yields metanitrobenzoic acid when heated at 235—240° with nitric acid of sp. gr. 1·15.

Metanitroisobutylbenzene, $C_4H_9{\cdot}C_6H_4{\cdot}NO_2$, obtained by treating the amido-derivative with nitrous acid, and fractionating the product in a partial vacuum, is a bright yellowish-red, aromatic-smelling oil, boiling at 250—252° (740 mm.). It yields metanitrobenzoic acid when heated at 200° with nitric acid of sp. gr. 1·12.

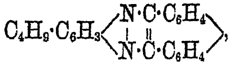
Nitroisobutylphenol, $[C_4H_9 : NO_2 : OH = 1 : 3 : 4]$, prepared by boiling amidonitroisobutylbenzene with dilute potash and distilling the product, separates from alcohol in yellowish-red, deliquescent crystals, melts at 95°, and boils at 289—290° (711 mm.) with only slight decomposition. It is readily soluble in alcohol, ether, benzene, light petroleum, alkalis, and hot water.

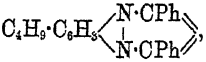
Metamidoisobutylbenzene, $C_4H_9{\cdot}C_6H_4{\cdot}NH_2$, prepared by reducing the nitro-derivative with stannous chloride and hydrochloric acid, is a yellowish oil, boiling at 229° (708 mm.), and moderately volatile with steam. It is readily soluble in alcohol, ether, and benzene, but only sparingly in water. It dissolves in a solution of bleaching powder with a bright violet colour, and with potassium dichromate and sulphuric acid yields a reddish-violet coloration, which quickly changes to brown. The *hydrochloride*, $C_{10}H_{15}N,HCl$, crystallises from hot benzene in colourless plates, and is readily soluble in water and hot alcohol, but only sparingly soluble in benzene. The *platinochloride*, $(C_{10}H_{15}N)_2,H_2PtCl_6$, crystallises in bright yellow plates, and is readily soluble in boiling water and hot alcohol, but only sparingly in benzene and ether. The *oxalate*, $C_{10}H_{15}N,C_2H_2O_4$, crystallises from hot water or dilute alcohol, in which it is readily soluble, in large white plates. The *acetyl*-derivative, $C_4H_9{\cdot}C_6H_4{\cdot}NHAc$, crystallises from boiling water in colourless, shining plates, melts at 101°, and is readily soluble in alcohol, ether, and benzene.

Metacetamidonitroisobutylbenzene, $[C_4H_9 : NO_2 : NHAc = 1 : 2 : 3]$, obtained by nitrating the acetamido-derivative, crystallises from hot dilute alcohol in small, yellow needles, melts at 105·5°, and is readily soluble in alcohol, benzene, and ether, but very sparingly in boiling water.

Amidonitroisobutylbenzene, $C_4H_9{\cdot}C_6H_3(NO_2){\cdot}NH_2$, separates from dilute alcohol in bright yellow crystals, melts at 124°, and is readily soluble in alcohol, ether, benzene, and boiling water, but sparingly soluble in cold water. It is only a feeble base, and the salts are readily soluble.

Diamidoisobutylbenzene, $[C_4H_9 : (NH_2)_2 = 1 : 2 : 3]$, prepared by reducing the preceding compound with stannous chloride and hydrochloric acid, crystallises from alcohol in colourless plates, melts at 109°, is readily soluble in water, alcohol, ether, and benzene, and blackens on exposure to the air. The *oxalate*, $(C_{10}H_{16}N_2)_2,C_2H_2O_4$, crystallises in flat needles, and is readily soluble in boiling water, but only sparingly in cold, absolute alcohol, and almost insoluble in ether.

Phenanthroisobutylphenazine,  $C_4H_9{\cdot}C_6H_3\left<\begin{matrix}N{\cdot}C{\cdot}C_6H_4\\ N{\cdot}C{\cdot}C_6H_4\end{matrix}\right>$, separates when an alcoholic solution of the diamine is mixed with a glacial acetic acid solution of phenanthraquinone. It separates from hot dilute alcohol in yellow nodular crystals, melts at 144° with previous softening, and is readily soluble in warm alcohol, ether, and benzene, but only sparingly in boiling water. It dissolves in concentrated nitric acid with a brownish-red, in concentrated sulphuric acid with a scarlet coloration, and is precipitated unchanged from both solutions on adding water.

Benzilisobutylphenazine,  $C_4H_9{\cdot}C_6H_3\left<\begin{matrix}N{\cdot}CPh\\ N{\cdot}CPh\end{matrix}\right>$, prepared in like manner from the diamine and benzil, crystallises in small, light-yellow prisms, melts at 96°, and is only sparingly soluble in cold alcohol, but readily in ether, benzene, and hot alcohol. It dissolves in concentrated nitric acid or concentrated sulphuric acid, but is precipitated unchanged on adding water.

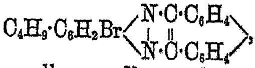
Acetamidobromonitroisobutylbenzene, $C_4H_9{\cdot}C_6H_2Br(NO_2){\cdot}NHAc$, prepared by nitrating acetamidobromisobutylbenzene, crystallises from a mixture of ether and light petroleum in small, rhombic plates, melts at 144°, and is readily soluble in hot alcohol, ether, or benzene, but only very sparingly soluble in boiling water.

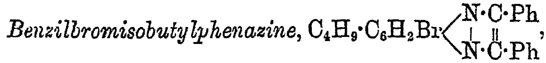
Amidobromonitroisobutylbenzene, $C_4H_9{\cdot}C_6H_2Br(NO_2){\cdot}NH_2$, crystallises in long needles, melts at 69·5°, boils at 278—280° with partial decomposition, and is volatile with steam. It is very sparingly soluble in boiling water, but readily in alcohol, ether, and benzene.

Diamidobromisobutylbenzene, $C_4H_9{\cdot}C_6H_2Br(NH_2)_2$, obtained by reducing the preceding compound with stannous chloride and hydrochloric acid, crystallises from ether in slender, colourless needles, melts at 85·5°, and turns brown on exposure to the air. It sublimes with considerable decomposition, forming colourless needles which are stable in the air. It is readily soluble in alcohol, ether, and benzene, but only very sparingly in hot water. Ferric chloride produces a brownish-red coloration; bleaching powder precipitates oily drops, and platinic chloride gives a brownish-black coloration in a hydrochloric acid solution of the base. The *oxalate*,

$$C_{10}H_{15}BrN_2,C_2H_2O_4,$$

crystallises in small needles, and is moderately soluble in boiling alcohol, but only sparingly in ether, benzene, and warm water. The *picrate*, $C_{10}H_{15}BrN_2{\cdot}2,C_6H_3N_3O_7$, crystallises from hot water in yellow needles, and is readily soluble in alcohol and ether.

Phenanthrobromisobutylphenazine,  $C_4H_9{\cdot}C_6H_2Br\left<\begin{matrix}N{\cdot}C{\cdot}C_6H_4\\ N{\cdot}C{\cdot}C_6H_4\end{matrix}\right>$, crystallises from boiling alcohol in slender, yellow needles, melts at 153·5°, and is readily soluble in benzene, ether, and boiling alcohol, but only sparingly in cold alcohol. It dissolves in concentrated mineral acids, forming red solutions, from which it is precipitated unchanged on adding water.



Benzilbromisobutylphenazine, $C_4H_9{\cdot}C_6H_2Br\left\langle\begin{array}{l}N{\cdot}C{\cdot}Ph\\ \;|\quad\|\\ N{\cdot}C{\cdot}Ph\end{array}\right.$, crystallises from hot alcohol in colourless needles, melts at 172°, and behaves towards solvents similarly to the preceding compound; it dissolves in concentrated acids with a yellowish-red coloration.

Dibromisobutylbenzene, $[C_4H_9 : Br_2 = 1 : 3 : 5]$, obtained by heating metabromisobutylbenzene with bromine in presence of iodine, and distilling the product with steam, is a light yellow oil, boils at 276—277° (718 mm.), and is readily soluble in all ordinary solvents except water. When heated at about 250° with nitric acid, sp. gr. 1·20, it is converted into symmetrical dibromobenzoic acid.

F. S. K.

Decomposition of some Diazo-compounds by Formic and Acetic Acids. By W. R. ORNDORFF (*Amer. Chem. J.*, **10**, 368—372).—The decomposition of diazo-compounds by formic acid might be expected to furnish an easier means of displacing the amido-group by hydrogen than the decomposition with alcohol. But the reaction proceeds otherwise and could not be followed out, as the phenyl formate that was probably formed could not be isolated. Substituting acetic acid for formic acid, it is shown that phenyl acetate is produced; the yield is, however, small, as much tar is also formed; the reaction is analogous to the production of phenetoïl by the action of alcohol. The boiling point of phenyl acetate has been variously stated; it has been redetermined as 195° at 733 mm. pressure. Similarly, paradiazotoluene sulphate, when boiled with acetic acid, yields paracresyl acetate, boiling at 213°, and identical with that prepared from paracresol. Paradiazobenzenesulphonic acid appears to undergo a similar change, and the reaction therefore seems to be general.

H. B.

Chrysoïdincarbamide. Amidophenylenecarbamide. By A. JENTZSCH (*J. pr. Chem.* [2], **38**, 121—139).—When carbonyl chloride is passed into a moderately strong solution of chrysoïdin in dry chloroform, it is rapidly absorbed with development of heat, and red-brown flocks separate which become of a darker brown as the action proceeds. The brown matter is collected, dried, powdered, heated with dilute hydrochloric acid, and filtered hot; brilliant golden-yellow laminæ crystallise out on cooling, together with octohedral crystals of diamidoazobenzene hydrochloride. By dissolving the mixed crystals in alcohol and adding ammonia, golden-yellow needles of the corresponding bases are obtained, which may be separated by digestion with chloroform, the diamidoazobenzene being dissolved. The residue, consisting of the new base, is purified by dissolving in alcohol and passing hydrogen chloride through the solution to obtain the hydrochloride which is then decomposed by ammonia.

Chrysoïdincarbamide, $NPh\!:\!NC_6H_3\!:\!(NH)_2\!:\!CO$, thus obtained, crystallises in brilliant, golden-yellow laminæ, sparingly soluble in alcohol, nearly insoluble in water, ether, and chloroform. It does not melt at 300°. If the chloroform solution of diamidoazobenzene be saturated with carbonyl chloride and allowed to stand for some days, only carbamide hydrochloride and unaltered chrysoïdin hydrochloride will be found on evaporating the chloroform. The *hydrochloride* crystallises in golden-yellow laminæ, sparingly soluble in water, more so in alcohol, insoluble in ether. The *platinochloride*, $(C_{13}H_{11}N_4OCl)_2PtCl_4$, forms red-brown laminæ. The *nitrate* crystallises in brilliant, golden-yellow scales, very sparingly soluble in water, sparingly soluble in alcohol, and insoluble in ether; they decompose with slight explosion at above 200°. The *sulphate* forms a yellowish-red powder; it is very sparingly soluble in water, more so in alcohol.

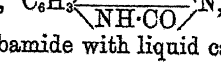
When heated with moderately strong hydrochloric acid in a sealed tube at 200° for eight hours, chrysoïdincarbamide is decomposed, with the formation of carbonic anhydride and a dark-brown mass. The same dark-brown substance is obtained when chrysoïdin is treated in the same way. It yields phenol when distilled with steam, and a reddish-brown residue which has not been identified.

Inasmuch as chrysoïdin splits up into aniline and triamidobenzene when reduced by hydrochloric acid and tin, it seemed probable that its carbamide would yield aniline and a new substance,

$$NH_2{\cdot}C_6H_3{:}(NH)_2{:}CO,$$

by the same treatment, thus showing that both NH-groups are attached to the same benzene nucleus. 100 grams of the carbamide were heated with 50 grams of tin and 250 grams of hydrochloric acid (sp. gr. 1·2) in a flask. The solution became colourless at first, and subsequently brown, through oxidation; after the action had ceased, the hydrochloric acid was evaporated, the residue dissolved in hot water, and hydrogen sulphide passed through the solution; the filtrate from the tin sulphide was evaporated in a current of hydrogen sulphide, the crystalline residue dissolved in water, and made alkaline with barium hydroxide. This precipitated aniline, which was distilled off; the excess of barium hydroxide was precipitated from the liquid remaining in the retort by sulphuric acid, and the excess of the latter by barium chloride. From the filtrate, the hydrochloride of the new base did not crystallise well, so the solution was digested with ammonium oxalate and filtered hot. On cooling, *amidophenylenecarbamide oxalate* crystallised out in nearly white minute needles, collected in spheres, freely soluble in hot, sparingly in cold water, nearly insoluble in alcohol.

Amidophenylenecarbamide, $NH_2{\cdot}C_6H_3{:}(NH)_2{:}CO$, obtained from the oxalate by adding sodium carbonate to a hot solution of it in hydrochloric acid, forms brilliant and nearly colourless, pointed laminæ, sparingly soluble in cold, easily in hot water, freely soluble in hot alcohol, and decomposing at 220°. The *hydrochloride* crystallises in minute needles, freely soluble in water, very sparingly so in alcohol. The *sulphate* also forms minute needles, having the same solubility. The *triacetyl-derivative*, $NHAc{\cdot}C_6H_3{:}(NAc)_2{:}CO$, forms fine, white, silky needles, insoluble in water, fairly soluble in alcohol, and melting at 248°.

Dicarbonyltriamidobenzene,  $C_6H_3{<}^{NH{\cdot}CO}_{NH{\cdot}CO}{>}N$, was obtained by heating amidophenylene carbamide with liquid carbonyl chloride in a sealed tube for eight hours at 120°. The excess of carbonyl chloride was evaporated and the residue heated with water, which extracted the hydrochloride of the carbamide formed during the reaction, and left the carbonyl compound as a crystalline residue, insoluble in alcohol, ether, benzene, toluene, aniline, and acids, but very soluble in alkaline solutions, from which it is precipitated by acids.

By passing nitrous acid through a cooled, acidified aqueous solution of the sulphate of amidophenylenecarbamide, yellowish-green crystals, giving the reactions of a diazo-compound of the carbamide, were obtained, but they were not pure. By dissolving them in hydrobromic acid and adding a few drops of bromine, yellowish-red needles of the perbromide of the diazo-compound crystallised out; these lost bromine as they dried, and by digesting them with warm alcohol they were converted into yellow crystalline laminæ of the *diazobromide* of amidophenylenecarbamide. A. G. B.

Hydrazoximes. By H. v. PECHMANN and K. WEHSARG (*Ber.*, 21, 2994 — 3004).—*Nitrosoacetonehydrazone* (*methylglyoxal-αω-hydrazoxime*) $N_2HPh{:}CMe{\cdot}CH{:}NOH$, prepared by mixing nitrosoacetone (1 mol.) with phenylhydrazine (1 mol.) in alcoholic or ethereal solution, crystallises from alcohol in yellowish prisms or needles, melts at 134°, and is soluble in ether and benzene, but insoluble in hot water. It dissolves in concentrated sulphuric acid with a reddish-yellow colour which becomes deep blue on adding ferric chloride.

Methylglyoxalosazone hydrochloride is obtained when the preceding compound is warmed with concentrated hydrochloric acid in alcoholic solution. It crystallises from boiling methyl alcohol, melts at 197°, and yields the free base (compare Abstr., 1888, 1287) when treated with ammonia.

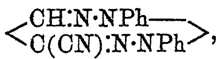
Diacetylhydrazoxime (*methylnitrosoacetonehydrazone*),

$$CMe(N_2HPh){\cdot}CMe{:}NOH,$$

prepared in like manner from nitrosomethylacetone, crystallises from dilute alcohol in large, colourless needles, melts at 158°, and resembles nitrosoacetonehydrazone in its behaviour towards solvents. It dissolves in concentrated sulphuric acid with a yellow coloration which changes to a bluish-violet on adding ferric chloride, and when heated with concentrated hydrochloric acid in alcoholic solution, yields a mixture of diacetylosazone melting at 241—242°, and diacetylhydrazone melting at 133°.

Glyoxylcyanide-α-hydrazone, $CHO{\cdot}C(N_2HPh){\cdot}CN$, is formed, together with hydroxylamine, when dinitrosoacetonehydrazone (compare this vol., p. 34) is warmed with alcohol and hydrochloric acid. It crystallises from boiling alcohol in pale-yellow needles, melts at 161° with decomposition, and is dissolved on warming in most solvents except water. It is soluble in dilute alkalis, and dissolves in concentrated sulphuric acid with a yellow colour which is not changed by ferric chloride. When boiled with hydriodic acid, it yields the theoretical quantity of aniline.

Glyoxylcyanideosazone, $N_2HPh{:}CH{\cdot}C(N_2HPh){\cdot}CN$, prepared by mixing a hot, alcoholic solution of the preceding compound with phenylhydrazine, crystallises from alcohol in orange-red needles, melts at 161° with decomposition, and is soluble in alcohol and glacial acetic acid, but only sparingly in most other solvents. The concentrated sulphuric acid solution is yellowish-red, and its colour is not changed by ferric chloride.

Glyoxylcyanideosotetrazone,  $\left\langle\begin{matrix}\mathrm{CH{:}N{\cdot}NPh}\text{——}\\ \mathrm{C(CN){:}N{\cdot}NPh}\end{matrix}\right\rangle$, is formed when the preceding compound is warmed with ferric chloride or with a solution of potassium dichromate and dilute acetic acid. It crystallises from acetone or alcohol in brownish-red, moss-like needles melting at 137° with decomposition. When heated with hydrochloric acid, a colourless, crystalline product, probably an osotriazone (*loc. cit.*) volatilises.

This compound, $C_9H_6N_3O{:}N_2Ph$, is formed by the combination of glyoxylcyanidehydrazone with diazobenzene chloride; it crystallises from alcohol in brownish plates, melts at 162—163°, and is insoluble in alkalis.

Glyoxylcyanide-αω-hydrazoxime, $NOH{:}CH{\cdot}C(N_2HPh){\cdot}CN$, prepared by boiling an alcoholic solution of the hydrazone (1 mol.) with hydroxylamine hydrochloride (1 mol.) and a few drops of hydrochloric acid, crystallises from alcohol in citron-yellow, sparingly soluble needles melting at 240° with decomposition. It dissolves in alkalis with a yellow coloration, but the yellow, concentrated sulphuric acid solution is not changed on adding ferric chloride.

A compound, $C_9H_7N_4$, is obtained when glyoxylcyanidehydrazoxime is dissolved in phosphorus oxychloride, heated with phosphoric chloride, the solution poured on to ice, the precipitated product extracted with ether, dissolved in dilute alkali, and fractionally precipitated with hydrochloric acid. It crystallises from a mixture of ether and light petroleum in yellowish needles, melts at 135° with decomposition, and is soluble in hot water, alkalis, and most of the ordinary solvents. It dissolves in concentrated sulphuric acid with a blood-red coloration which is not changed on adding ferric chloride. When warmed with concentrated hydrochloric acid or when boiled with alcoholic potash, it is converted into a compound, $C_9H_9N_4O$, which crystallises in small, yellow needles melting at 244—245°.

A compound, $C_{15}H_{13}N_5$, is formed in the preparation of glyoxylcyanidehydrazone, and can also be obtained by heating the hydrazoxime with alcohol (3 parts) and concentrated hydrochloric acid (10 parts). It crystallises from benzene in shining, orange-yellow plates melting at 165°, and does not give the osazone reaction (*loc. cit.*).

Methylglyoxal-αω-methylphenylhydrazoxime, $N_2MePh{:}CMe{\cdot}CH{:}NOH$, prepared by mixing an aqueous solution of nitrosoacetone with a solution of methylphenylhydrazine sulphate and sodium acetate, crystallises from dilute alcohol in orange-yellow prisms melting at 118°. Alkaline solutions are dark yellow, and the yellow, concentrated sulphuric acid solution changes to violet on adding ferric chloride.

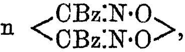
Mesoxalaldehyde-αωω-methylphenylhydrazonedioxime (*dinitrosoacetonemethylphenylhydrazone*), $NOH{:}CH{\cdot}C(N_2MePh){\cdot}CH{:}NOH$, prepared in like manner, crystallises from dilute alcohol in orange-yellow needles or plates, melts at 137°, and is soluble in alkalis and most of the ordinary solvents. It dissolves in concentrated sulphuric acid, forming a brownish-red solution in which ferric chloride produces a light violet coloration. When heated with hydrochloric acid, it yields decomposition products the nature of which varies according to the conditions of the experiment.

Glyoxylcyanide-α-methylphenylhydrazone, $CHO\cdot C(N_2MePh)\cdot CN$, is obtained by dissolving the preceding compound in acetone (7 parts), adding concentrated hydrochloric acid (7 parts) and, after the first energetic reaction is at an end, heating the mixture for about a minute and adding water to the cold solution. It crystallises from benzene, alcohol, or light petroleum in yellow, feathery needles, or thick, spear-shaped crystals, melts at 113·5°, and is insoluble in alkalis. When mixed with phenylhydrazine, it yields a compound, probably $N_2HPh:CH\cdot C(N_2MePh)\cdot CN$, which crystallises from absolute alcohol in golden-yellow plates melting at 181°. The *anil*, $NPh:CH\cdot C(N_2MePh)\cdot CN$, prepared by mixing the hydrazone with aniline in acetic acid solution, crystallises from alcohol in slender, yellow needles, melts at 150—151°, and is reconverted into the hydrazone when warmed with dilute hydrochloric acid. The *hydrazoxime*, $NOH:CH\cdot C(N_2MePh)\cdot CN$, obtained by treating the hydrazone with hydroxylamine, crystallises in small, yellow needles melting at 178°. The *acetyl*-derivative, $NOAc:CH\cdot C(N_2MePh)\cdot CN$, of the hydrazoxime crystallises from alcohol in yellow needles, melts at 121·5°, and is reconverted into the hydrazoxime when boiled with soda. F. S. K.

Ethyl Phenylhydrazineacetylacrylate. By H. Decker (*Ber.*, **21**, 2937—2938).—The compound obtained by Bender (Abstr., 1888, 1188) by hydrolysing ethyl phenylhydrazineacetylacrylate, has already been fully described by L. Wolff (Abstr., 1887, 464). F. S. K.

Theory of Dyeing. By E. Knecht (*Ber.*, **21**, 2804—2805; compare Abstr., 1888, 832).—When wool is boiled with a mixture of sulphuric acid (2 parts) and water (3 parts) for two hours, it dissolves almost entirely; when filtered, a clear, light-brown solution is obtained. If this is mixed with aqueous solutions of acid coal-tar dyes, intensely coloured precipitates are formed, which dissolve readily in alkalis, but not in water or dilute acids.

A solution of silk in moderately dilute sulphuric acid behaves in like manner. Animal fibres, therefore, yield a substance which forms insoluble bases with acid coal-tar dyes; it has not yet been determined whether this substance already exists in the fibres, or whether it is gradually formed by the action of the acid bath. N. H. M.

Product of the Action of Nitric Acid on Acetophenone. By A. F. Hollemann (*Ber.*, **21**, 2835—2840; compare Abstr., 1888, 275).—The molecular weight of the compound $C_{16}H_{10}N_2O_4$, obtained by the action of nitric acid on acetophenone (*loc cit.*), was confirmed by a determination by Raoult's method (*Ber.*, **21**, 861). When the alcoholic solution is reduced with stannous chloride, benzoic and hydrocyanic acids are formed. By prolonged boiling with strong hydrochloric acid, it is decomposed into benzoic and oxalic acids; ammonia and hydroxylamine are also formed. These reactions make it probable that the compound has the constitution  $<\begin{matrix}\mathrm{CBz{:}N{\cdot}O}\\\mathrm{CBz{:}N{\cdot}O}\end{matrix}>$, which is further supported by the fact that the substance, which is named *diphenyldinitrosacyl*, can be prepared by oxidising nitrosoacetophenone.

Diphenyldinitrosacyl reacts with aniline with formation of benzanilide and a compound crystallising in lustrous, brown needles. When this is heated at 100° for some time, it gives an odour somewhat like that of carbylamine: when crystallised from dilute alcohol, it is nearly white, and melts at 205°.

When diphenyldinitrosacyl is heated with acetic anhydride at 110—120° for six hours, the compound $C_{16}H_{10}N_2O_4 + OAc_2$ is formed. This crystallises in stellate groups of needles melting at 149°.

The sparingly soluble compound melting at 177—179°, which is also obtained by the action of nitric acid on acetophenone (*loc. cit.*), has the same empirical composition as diphenyldinitrosacyl; it is, however, much more stable than the latter. Boiling aqueous potash and hot sulphuric acid decompose it, yielding benzoic acid; with potash, ammonia is evolved. N. H. M.

Consecutive Duryl Methyl Ketone. By A. CLAUS and E. FÖHLISCH (*J. pr. Chem.* [2], **38**, 230—235; compare Abstr., 1888, 275).—The boiling point of consecutive durene is 199—200° (uncorr.) and its melting point is −4°.

Consecutive duryl methyl ketone, $C_6HMe_4{\cdot}COMe$ [Me_4 : COMe = 2 : 3 : 4 : 5 : 1], is prepared in the manner previously described, by which 80—90 per cent. of the durene used is converted into the ketone; it is a brown, strongly refractive oil, of agreeable aromatic odour, boiling at 258—260° (uncorr.), and easily soluble in the usual solvents, except water. The *phenylhydrazine* compound forms colourless laminæ melting at 129° (uncorr.).

2 : 3 : 4 : 5-*Tetramethylphenylglyoxylic acid*, $C_6HMe_4{\cdot}CO{\cdot}COOH$, is formed when the above ketone is oxidised with potassium permanganate in the cold. It is a bright yellow syrupy oil, very little soluble in cold, more so in hot water, very soluble in alcohol, ether, carbon bisulphide, and chloroform; it solidifies on prolonged cooling and decomposes when heated. The *barium* and *calcium salts* (with 4 mols. H_2O), the *copper* (with 3 mols. H_2O), and the *silver salts* are described.

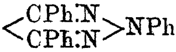
2 : 3 : 4 : 5-*Tetramethylmandelic acid*, $C_6HMe_4{\cdot}CH(OH){\cdot}COOH$, is obtained by reducing the foregoing acid with sodium amalgam. It crystallises from alcohol in colourless hexahedra, sparingly soluble in cold, readily in hot water and in alcohol, ether, and chloroform, and melts at 160° (uncorr.). The *potassium* (with 4 mols. H_2O), *barium* (with 3 mols. H_2O), *calcium* (with $2\frac{1}{2}$ mols. H_2O), and *silver* salts are described.

2 : 3 : 4 : 5-*Tetramethylphenylacetic acid*, $C_6HMe_4{\cdot}CH_2{\cdot}COOH$, is formed when either of the above described acids is reduced with

hydriodic acid. It crystallises from hot water in slender, colourless needles, melting at 125° (uncorr.), and easily soluble in alcohol, ether, and chloroform. The *calcium salt* forms colourless, silky needles containing 3 mols. H_2O.

By oxidising consecutive duryl methyl ketone or the foregoing derivatives, with the calculated quantity of potassium permanganate, at a gentle heat, 2 : 3 : 4 : 5- tetramethylbenzoic acid is obtained as a thick, colourless oil, sparingly soluble in water, freely so in other solvents. When heated, it decomposes at 270°, and an oil distils over, which solidifies and melts at 150°; this contains 73·8 per cent. of carbon and 7·9 per cent. of hydrogen. The *sodium* (with 3 mols. H_2O), *calcium* (with 3 mols. H_2O), *barium* (with 6 mols. H_2O), *silver* and *copper salts* are described. A. G. B.

Stilbene. By L. ARONSTEIN and A. F. HOLLEMANN (*Ber.*, **21**, 2831—2834).—The experiments described were made with a view to obtain a geometrical isomeride of stilbene which should exist according to Wislicenus' theory. No definite results were obtained, but the investigation is being continued. N. H. M.

Action of Heat on Benzildihydrazone. By K. AUWERS and V. MEYER (*Ber.*, **21**, 2806—2807).—*Triphenylosotriazone*,  $<\begin{matrix}CPh{:}N\\CPh{:}N\end{matrix}>NPh$, formed when benzilhydrazone is heated with alcohol at 200—210°, crystallises in white, lustrous plates, melts at 122°, and boils without decomposition. N. H. M.

Thio-derivatives of β-Dinaphthylamine. By O. KYM (*Ber.*, **21**, 2807—2813).—When sulphur chloride dissolved in benzene is added to β-dinaphthylamine, also dissolved in benzene, hydrogen chloride is evolved and two isomeric *dithiodinaphthylamines*, $C_{20}H_{13}NS_2$, are obtained. The one forms lustrous, brass-coloured plates melting at 205°, whilst the other crystallises in reddish-yellow prisms melting at 220°. Both compounds are sparingly soluble. When the dithio-compounds are boiled with cumene or with aniline, they are both converted with evolution of carbon bisulphide into Ris's thio-β-dinaphthylamine (Abstr., 1886, 1036). A small quantity of the latter compound is formed in the reaction between dinaphthylamine and sulphur chloride. *Acetylthio-β-dinaphthylamine*, $C_{22}H_{15}NOS$, is obtained by the action of acetic anhydride on the dithio-compound (m. p. 205°) or on the monothio-compound. It crystallises in slender, lustrous, almost white needles, melts at 211°, and is readily soluble in hot alcohol or benzene. When the dithio-compound (m. p. 205°) is treated with an ammoniacal alcoholic silver solution, a compound free from sulphur is obtained, which melts at 240°, and sublimes in slender, lemon-yellow needles.

Sulphur dichloride acts on β-dinaphthylamine, yielding as chief product thio-β-dinaphthylamine, and a sparingly soluble isomeride which melts at 303°. Sometimes a small amount of a compound, probably *thiotetranaphthylamine*, $S(C_{10}H_6{\cdot}NH{\cdot}C_{10}H_7)_2$, is obtained. This forms dark-yellow crystals melting at 307°. N. H. M.

Naphthoic Acids. By Å. G. Ekstrand (*J. pr. Chem.* [2], **38**, 139—185).—This paper is a summary of the author's work on the subject; much of it has already appeared. The following new compounds are described:—

Chloro-α-naphthoic amide is obtained by heating chloro-α-naphthonitrile (Abstr., 1884, 1361) with an alcoholic solution of potassium hydroxide; it forms crystalline laminæ, soluble in alcohol and melting at 239°.

The chloro-α-naphthoic acid which melts at 245° (Abstr., 1884, 1361) has the constitution [COOH : Cl = 1 : 4′], as it is obtained by treating 1 : 4′ amido-α-naphthoic acid by Sandmeyer's method (Abstr., 1884, 1311).

Chloro-α-naphthoic acid (1 : 1′) is obtained when 1 : 1′ amido-α-naphthoic acid (Abstr., 1885, 549) is dissolved in the calculated quantity of sodium hydroxide and potassium nitrite (1 mol. to 1 mol. of the amido-acid) added; the mixture is cooled to 0° and treated with excess of hydrochloric acid. The hydrochloride of the diazonaphthoic acid thus obtained is added to a boiling solution of cuprous chloride in hydrochloric acid; colourless crystals of the chloro-acid are formed; they melt at 167° and sublime as plates. The *calcium salt* crystallises with 2 mols. H_2O in long tabular needles, soluble in 42 parts of water at the ordinary temperature. The *ethyl salt* forms long needles melting at 50°.

Dichlor-α-naphthoic acid is obtained when the foregoing acid is dissolved in glacial acetic acid, some iodine added, and chlorine passed to saturation; crystalline scales separate, melting at 186—187°. The *calcium salt* crystallises with 2 mols. H_2O in long, colourless needles; the *ethyl salt* forms fine needles melting at 61°.

It is possible to obtain this acid from chlornitro-α-naphthoic acid [COOH : NO_2 : Cl = 1 : 1′ : 4′] (Abstr., 1886, 156), consequently its constitution is [COOH : Cl : Cl = 1 : 1′ : 4′].

Trichloro-α-naphthoic acid, the mother-liquor from the preparation of chloro-α-naphthoic acid (1 : 4′) by the action of chlorine on α-naphthoic acid in acetic acid solution, is saturated with chlorine at the boiling point; dilution with water then throws down a crystalline precipitate, which is heated with calcium carbonate, filtered, and the filtrate precipitated with acid; when crystallised from alcohol and water, this precipitate forms small, colourless needles, melting at 163—164° and subliming in fine needles.

The *ethyl salt* of monobromo-α-naphthoic acid, 1 : 4′ (Abstr., 1886, 715), forms colourless tables melting at 48—49°.

Mononitro-α-naphthoic acid of melting point 215° (Abstr., 1885, 548) is soluble in 21·5 parts of commercial alcohol, and in 2590 parts of water at the ordinary temperature. During its formation a small quantity of *α-mononitronaphthalene* (melting point 60°) is obtained.

The *calcium salt* of amido-α-naphthoic acid (Abstr., 1885, 549) crystallises with 9·5 mols. H_2O in fine needles, soluble in water. The *hydrochloride*, $COOH{\cdot}C_{10}H_6{\cdot}NH_2,HCl$, is precipitated in fine needles on adding hydrochloric acid to a solution of the sodium salt.

Naphthostyril, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}$ (Abstr., 1886, 715), crystallises from an alcoholic solution of the amido-α-naphthoic acid; it is also formed when the acid is heated with water; it melts at 180—181°.

The *benzoyl-derivative* forms slender needles melting at 170°; the *hydrochloride* melts at 178°.

α-Naphthoylnaphthostyril.—When α-naphthoyl chloride and naphthostyril are heated together, a green product is formed, which is dissolved in alcohol and decolorised by animal charcoal. A mixture of granular crystals (melting at 110°) and needles (melting at 152°) is obtained; by recrystallising these, partly from alcohol and partly from glacial acetic acid, a mixture of the same crystals is obtained, melting at 150°.

β-Naphthoylnaphthostyril, is obtained in the same way as the above, only at a lower temperature, in slender colourless needles, melting at 197—198°.

The *calcium salt* of chlornitro-α-naphthoic acid, of melting point 225° (Abstr., 1886, 156), forms slender colourless needles, crystallising with 3 mols. H_2O, and the *ethyl salt* tabular crystals melting at 121°, and very soluble in alcohol. The question whether this acid has the constitution [COOH : NO_2 : Cl = 1 : 1′ : 4′ or 1 : 4 : 4′] is settled in favour of the former, as *chloronaphthostyril* (with Cl in position 4′) is obtained in yellow needles melting at 270°, by reducing the acid with ferrous sulphate in an ammoniacal solution.

Nitronaphthostyril (1 : 4′) is formed when nitric acid (sp. gr. 1·42) is added to a solution of naphthostyril in glacial acetic acid, and the mixture heated on the water-bath; the crystalline mass thus obtained is partially soluble in alcohol, from which yellow needles, melting about 235°, are obtained; the greater part recrystallises from glacial acetic acid in orange-yellow needles melting at 300°. Both are nitronaphthostyrils.

Amidonaphthostyril is formed when nitronaphthostyril is reduced with tin and hydrochloric acid, and the hydrochloride thus produced decomposed with ammonia; it crystallises in red needles melting at 239—240°, and freely soluble in alcohol and hot water. The *hydrochloride* crystallises in yellow needles melting above 290°.

Dinitronaphthostyril is obtained when the nitronaphthostyril is heated with nitric acid (1·43 sp. gr.); it forms yellow needles, or, when prepared by the action of nitric acid on naphthostyril, rhombic tables, melting above 290°. The *acetyl*-derivative melts above 290°.

Naphthostyrilquinone, $C_{10}H_4O_2<\substack{NH \\ CO}>$, is obtained when a solution of naphthostyril in glacial acetic acid is mixed with chromic acid and then with water; fine red needles are precipitated, which, after recrystallisation from glacial acetic acid, melt near 278°. When it is dissolved in warm glacial acetic acid and an acetic acid solution of toluylenediamine added, a yellow, crystalline powder, consisting of *naphthostyriltoluquinoxaline*, $C_{11}H_5N_3O,C_6H_3CH_3$, is obtained; it melts above 290°.

Nitronaphthostyrilquinone forms orange-red needles or tables, melting near 285°, soluble in alcohol and sparingly so in glacial acetic acid.

A. G. B.

β-Chloronaphthalenesulphonic Acid. By S. FORSLING (*Ber.*, **21**, 2802—2804).—When β-amidonaphthalenesulphonic acid (Abstr., 1887, 962) is converted into the diazo-compound, and this is boiled with strong hydrochloric acid and neutralised with potassium carbonate, potassium β-chloronaphthalenesulphonate separates.

β-Chloronaphthalenesulphonic chloride, $C_{10}H_6Cl{\cdot}SO_2Cl$ (Arnell, Abstr., 1886, 555), is prepared by mixing the well-dried potassium salt with phosphorus pentachloride and heating; it crystallises from chloroform in broad needles melting at 129°.

The *bromide*, $C_{10}H_6Cl{\cdot}SO_2Br$, prepared by the action of phosphorus bromide on the potassium salt, crystallises from chloroform in small needles melting at 139°.

The *amide*, $C_{10}H_6Cl{\cdot}SO_2{\cdot}NH_2$, is obtained by boiling the chloride with a mixture of equal parts of ammonia and alcohol, and crystallising the product from dilute alcohol, in which it is sparingly soluble; it melts at 235°.

β-Chloronaphthalenesulphonic acid has the constitution [Cl : SO_3H = 2 : 4 or 2 : 1]. N. H. M.

Filicic Acid. By G. DACCOMO (*Ber.*, **21**, 2962—2970).—Filicic acid, prepared by the method already described (Daccomo, Abstr., 1888, 521), has the composition $C_{14}H_{16}O_5$. It is a yellowish, odourless, crystalline powder, melts at 179—180° (uncorr.), and is insoluble in water, almost insoluble in absolute alcohol, moderately soluble in glacial acetic acid, ether, amyl alcohol, and toluene, and readily in chloroform, carbon bisulphide, and benzene. The *benzoyl*-derivative, $C_{21}H_{20}O_6$, separates from dilute alcohol in colourless crystals, melts at 123°, and is very readily soluble in ether, but insoluble in water. The *ethyl* salt, $C_{16}H_{20}O_5$, prepared by treating the acid with alcoholic potash and ethyl iodide, separates from dilute alcohol in reddish crystals, melts at 142°, and is very readily soluble in ether and benzene, but insoluble in water. The *propyl* salt melting at 158°, and the *ethylene* salt melting at 165°, resemble the ethyl salt in appearance and solubility.

Bromofilicic acid, $C_{14}H_{15}BrO_5$, prepared by treating the acid with bromine in glacial acetic acid solution, crystallises from alcohol in red prisms, melts at 122°, and is very readily soluble in absolute alcohol and ether, but insoluble in water.

Anilidofilicic acid, $C_{14}H_{15}O_4{\cdot}NHPh$, obtained by boiling a glacial acetic acid solution of the acid with aniline, separates from alcohol in reddish-violet crystals, melts at 140°, and is soluble in alcohol and benzene, but insoluble in water.

The *hydrazide*, $C_{14}H_{16}O{\cdot}(N_2HPh)_4$, prepared by boiling an ethereal solution of the acid with phenylhydrazine, crystallises from ether in red needles, melts at 198°, and is readily soluble in alcohol, but insoluble in water. When the acid (100 parts) is heated above its melting point (compare Luck, *Annalen*, **54**, 119), or heated with water at 170—190°, it is decomposed into isobutyric acid (32·5 parts) and a compound, the composition of which is $C_{20}H_{18}O_7$. Hydrochloric acid produces the same decomposition at 150—160°.

Filicic acid is completely oxidised when treated with chromic acid in glacial acetic acid solution, but when a solution of the potassium salt is oxidised in the cold with a 2 per cent. solution of potassium permanganate, isobutyric acid and oxalic acid are obtained. The same products are formed when nitric acid of sp. gr. 1·48 is employed. When the acid is treated with zinc-dust in alkaline solution, it is converted into an acid, the composition of which is probably $C_{14}H_{22}O_{11}$, and at the same time a small quantity of isobutyric acid is formed. When treated with sodium in amyl alcohol solution, it yields butyric acid and resinous products.

The compound $C_{20}H_{18}O_7$, referred to above, separates from ether or amyl alcohol as an amorphous, red powder, and has no well-defined melting point. It is soluble in most ordinary solvents, has an acid reaction, decomposes carbonates, and dissolves in alkalis, forming red solutions from which it is precipitated in red flocks on adding acids. It yields phthalic acid and small quantities of oxalic acid when oxidised with nitric acid of sp. gr. 1·40 in the cold. When reduced with zinc-dust in alkaline solution, it gives a colourless substance which rapidly oxidises, and is probably reconverted into the original compound.

From the above results, it follows that filicic acid is probably an isobutyric acid derivative of hydroxynaphthaquinone. F. S. K.

Quillajic Acid. By R. KOBERT (*Chem. Centr.*, 1888, 927—928, from *Arch. expt. Path. Pharm.*, **23**, 233).—The saponin of commerce, as all other specimens of saponin, is an almost inactive, non-poisonous modification of quillajic acid. The author precipitated the acid from the aqueous extract of the bark of *Quillaja saponaria* with neutral lead acetate; the precipitate was freed from lead, the solution of the acid evaporated almost to dryness, and then taken up with hot absolute alcohol. The colouring matter was precipitated with chloroform; the quillajic acid eventually crystallised out in pure white flakes. It is insoluble in ether, soluble in water and alcohol. On treatment with concentrated sulphuric acid, it becomes dark red. By boiling with dilute mineral acids, it is split up into an unfermentable glucose and sapoginin; this solution reduces Fehling's solution. Quillajic acid has the formula $C_{19}H_{30}O_{10}$. The sodium salt acts as a very severe caustic on the tongue and throat, and the smallest particles coming in contact with the nose or throat cause violent sneezing and coughing. Brought on to the eye, it causes severe pain, flow of tears, and swelling of the lids. Injected into the blood, the sodium salt proves fatal, causing cramp and paralysis of the respiratory organs and brain. On the other hand, it may be imbibed into the stomach without injury to the extent of 500 times the quantity which proves fatal when injected into the blood. J. W. L.

Brazilin. By C. SCHALL and G. DRALLE (*Ber.*, **21**, 3009—3017, compare Abstr., 1888, 295).—Tetramethylbrazilin is best prepared as follows:—A solution of brazilin (100 grams) in warm 98 per cent. alcohol is mixed with sodium ethoxide (30·26 grams sodium) and methyl iodide (206 grams), the mixture kept at 60—70° for 40 to 50 hours, cooled and poured into cold water. The precipitate is collected, washed with water, dissolved in ether, the solution shaken with soda (1—2 per cent.), washed with water, the ether evaporated, and the residue crystallised from alcohol with addition of animal charcoal. The yield is 58·5 per cent. of the theoretical quantity.

Trimethylbrazilin, $C_{16}H_{11}O_5Me_3 + \frac{3}{4}H_2O$, is obtained by neutralising the alkaline washings from the tetramethyl-derivative, extracting with ether, washing the extract first with sodium hydrgen carbonate, then with sodium carbonate, and evaporating the ether at the ordinary temperature. The residue is mixed with concentrated soda, the precipitated sodium-derivative collected, washed with alcoholic ether, dissolved in water, and precipitated from the filtered solution by treatment with carbonic anhydride. If the product is pure, it is obtained in the crystalline condition containing about 1 mol. H_2O, but the impure compound does not crystallise well even after keeping for months. It dissolves in dilute alcohol, and the solution gives a brown precipitate with ferric chloride; the solution in soda is colourless, and does not alter on keeping. The *acetyl*-derivative, $C_{16}H_{10}O_5Me_3Ac$, is crystalline, and melts at 95—97° with previous softening.

Bromotetramethylbrazilin, $C_{16}H_9BrMe_4O_5$, obtained by treating the tetramethyl-derivative (1 mol.) with bromine (1 mol.) in glacial acetic acid solution, crystallises from dilute alcohol in long, colourless prisms melting at 180—181°.

A crystalline tetrabromo-derivative, $C_{16}H_8Br_4Me_4O_5$, is formed when a larger quantity of bromine (2—3 mols.) is employed; this substance loses bromine (about 26 per cent.) when treated with dilute ammonia or soda, and appears to be dibromotetramethylbrazilin dibromide. It is probable that other bromo-derivatives exist, and a crystalline iodo-additive product was also obtained.

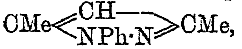
Tribromobrazilin dibromide, $C_{16}H_{11}Br_3O_5,Br_2 + 2H_2O$, is obtained in reddish-brown needles when bromine (4—6 mols.) is added gradually to a boiling glacial acetic acid solution of brazilin.

A compound, $C_{20}H_{14}O_9$, is obtained when brazilin (2·7 grams) is dissolved in water (150 c.c.) and soda of sp. gr. 1·37 (10 c.c.), and a stream of air passed through the solution for about 36 hours. It crystallises from alcohol in light brown, flat, microscopic needles, melts at 271°, and is readily soluble in dilute soda, sparingly soluble in ether or sodium carbonate, and insoluble in sodium bicarbonate. The aqueous alcoholic solution gives a slight violet coloration with ferric chloride, and a citron-yellow coloration with concentrated nitric acid. When heated above its melting point, shining scales sublime, but considerable decomposition takes place. F. S. K.

Nomenclature of Compounds containing Nitrogenous Nuclei. By O. Widman (*J. pr. Chem.* [2], **38**, 185—201).—A new system of nomenclature for the quinoxalines and compounds of allied structure. (Compare Mason, Proc., 1888, 109.)

Metapyrazolones. By E. Grimaux (*Bull. Soc. Chim.*, **49**, 739—740).—The compounds described by Pinner and Lifschütz, and named by them metapyrazolone-derivatives, are derivatives of glycolylcarbamide or hydantoïn, and the isomeric substances which Pinner and Lifschütz name metapyrazole-derivatives are simple ureïdes.

F. S. K.

Action of Phenylhydrazine and Hydroxylamine on Acetylacetone. By A. Combes (*Bull. Soc. Chim.*, **50**, 145—146; compare *ibid.*, **48**, 471).—*Dimethylphenylpyrazole*,  $\mathrm{CMe}\lessdot\begin{matrix}\mathrm{CH}\text{——}\\ \mathrm{NPh\cdot N}\end{matrix}\gtrdot\mathrm{CMe}$, is formed by the action of phenylhydrazine on acetylacetone: it boils at 270·5°. (Compare Claisen, Abstr., 1888, 692; and Zedel, 1051.)

N. H. M.

Derivatives of Methylpyrroline. By G. de Varda (*Ber.*, **21**, 2871—2874).—*Methyltetrabromopyrroline*, C_4NBr_4Me, obtained by digesting tetrabromopyrroline with caustic alkali and methyl iodide dissolved in methyl alcohol, crystallises from light petroleum in long, colourless needles, which melt at 154—155° to an intensely blue liquid.

Dibromomaleïnmethylimide, $C_4Br_2O_2NMe$, is prepared by slowly adding the above tetrabromide to fuming nitric acid (3 parts), cooled to 0°, and pouring the product into water (10 parts). It crystallises from boiling water in long, light-yellow needles melting at 121°. It distils readily with steam; the vapour has an irritating odour.

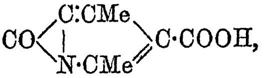
Methylpyrrylglyoxylic acid, $C_4NH_3Me{\cdot}CO{\cdot}COOH$, is obtained by treating a boiling solution of methylacetylpyrroline (5 grams) in alkaline water (500 c.c.) with a solution of potassium permanganate (15·5 grams) in water (500 c.c.). The whole is boiled, steam-distilled, and filtered; it is then evaporated down, acidified, and extracted with ether. The acid is crystallised from benzene, from which it separates in light-yellow needles which melt at 141—142·5° with decomposition; it is sparingly soluble. The *silver salt* was prepared. The *dibromo-derivative*, $C_4NHMeBr_2{\cdot}CO{\cdot}COOH$, prepared by brominating the acid dissolved in acetic acid, crystallises from benzene in small, sulphur-coloured prisms melting at 160°. When the dibromo-acid is slowly added to fuming nitric acid (10 parts), dibromomaleïnmethylimide is formed. The bromine-atoms and the $—CO{\cdot}COOH$ group have, therefore, the positions 3, 4, and 5 respectively.

N. H. M.

Derivatives of Unsymmetrical Dimethylpyrroline. By G. Magnanini (*Ber.*, **21**, 2864—2868, 2874—2879).—*Ethyl dimethylacetylpyrrolinecarboxylate*, $C_4NHMe_2Ac{\cdot}COOEt$ [2 : 4 : 5 : 3], prepared by heating ethyl hydrogen dimethylpyrrolinedicarboxylate (Knorr, *Annalen*, **236**, 318) with acetic anhydride at 200°, crystallises in needles, melts at 142—143°, dissolves very readily in alcohol, ether, acetic acid, and benzene, &c., sparingly in light petroleum. The *free acid* obtained by boiling the ethyl salt with aqueous potash, melts at about 152—158° with formation of *dimethylacetylpyrroline* and evolution of carbonic anhydride, is almost insoluble in boiling water, very sparingly soluble in ether, chloroform, and benzene, and readily soluble in hot acetic acid, from which it separates in long, lustrous needles. It gives a green coloration when heated with isatin and sulphuric acid.

Dimethylacetylpyrroline, $C_4NH_2Me_2Ac$ [= 2 : 4 : 5], is prepared by distilling dimethylacetylcarbopyrrolic acid in a retort heated in a metal-bath at 200°. It is first crystallised from water containing a little sodium carbonate, then from dilute alcohol, and lastly from light petroleum. It melts at 122—123°, sublimes at 100°, and is readily soluble in the usual organic solvents.

Dimethylpyrrolinedicarboxylic acid imineanhydride,



$$CO\left\langle\begin{matrix}C{:}CMe\\ |\\ N{\cdot}CMe\end{matrix}\right\rangle C{\cdot}COOH,$$

is obtained by boiling Knorr's unsymmetrical dicarboxylic acid (Abstr., 1887, 275) with acetic anhydride (10 parts) in a reflux apparatus for three to four hours. The acetic anhydride is distilled off under diminished pressure, the residue washed with alcohol, dissolved in aqueous sodium carbonate, filtered, and precipitated with acetic acid. It is almost insoluble in the usual solvents, becomes slightly brown at 300°, and decomposes at a higher temperature into dimethylpyrroline and dimethylpyrocoll. It resists the action of mineral acids, but seems to be partially decomposed by aqueous ammonia. The *silver salt* is a yellowish, amorphous substance; the *magnesium salt* forms lustrous needles. The *ethyl salt* crystallises in thread-like needles, melts at 270°, and is sparingly soluble.

2, 4-*Dimethylpyrocoll*, C_7H_7NO, obtained by distilling the copper or silver salt of the above acid in a stream of carbonic anhydride, is light yellow, melts at 272—272·5°, dissolves very readily in chloroform, readily in acetic acid, but only sparingly in ether, light petroleum, and cold alcohol; it is insoluble in water. The crystals are rhombic; $a : b : c = 0{\cdot}78834 : 1 : 0{\cdot}94602$. The compound is hardly attacked by aqueous potash. N. H. M.

Derivatives of Pyrrolinephthalide. By F. Anderlini (*Ber.*, **21**, 2869—2870).—*Dibromopyrrolinephthalide*, $C_{12}H_5Br_2NO_2$, prepared by treating a warm solution of pyrrolinephthalide (2 grams) in glacial acetic acid (15 grams) with bromine (8 grams), crystallises in small, yellow, lustrous needles, melts at 199°, is insoluble in water, sparingly soluble in boiling alcohol and ether.

Nitropyrrolinephthalide, $C_{12}H_6N_2O_4$, is formed when the phthalide is dissolved in strong nitric acid; it crystallises from alcohol in needles. When pyrrolinephthalide is treated with bromine in alkaline solution, tetrabromopyrroline and phthalic acid are formed. On similarly treating the dibromo- and nitro-derivatives, both compounds yield phthalic acid; the substituted radicles are therefore in the pyrroline nucleus.

When potassium pyrrolinephenylcarbinolorthocarboxylate,

$$C_4NH_3{:}C(OH){\cdot}C_6H_4{\cdot}COOK,$$

is distilled with potassium carbonate, it is decomposed into pyrroline and benzene. N. H. M.

Action of Methyl Iodide on some Pyrroline-derivatives. By G. Ciamician and F. Anderlini (*Ber.*, **21**, 2855—2864).—*Dihydrotetramethylpyridine*, $C_9H_{15}N$, is obtained, together with other bases, when sodium carbopyrrolate (5 grams), methyl iodide (10 grams), and methyl alcohol (7 grams) are heated at 120° for 12 hours. It boils at about 160°. The *aurochloride*, $C_9H_{15}N,HAuCl_4$, crystallises from very dilute solutions in long, flat, monoclinic needles; $a : b : c = 5\frac{1}{3} : 10 : 5\frac{1}{4}$; $\beta = 85\frac{4}{5}$. When the base is reduced with sodium and alcohol, the compound $C_9H_{19}N$ is formed. This boils at 150—152°. The *aurochloride* separates from its solution as an oil, which crystallises after some days in yellow needles melting at 117—119°. When the base $C_9H_{19}N$ is boiled with methyl iodide in a reflux apparatus, and the product, freed from the excess of methyl iodide, is dissolved in alcohol and precipitated with ether, the compound $C_{19}H_{18}NMe_2I$ is obtained in colourless prisms which melt at 262°. It is very readily soluble in water, insoluble in ether. The mother-liquor from the dimethyl compound contains a small amount of a *base*, $C_9H_{18}NMe$, which forms an oil.

Methyldihydropyrroline, $C_{10}H_{17}N$, is prepared by heating methylpyrroline (3 grams), methyl iodide (7 grams), potassium carbonate (3 grams), and methyl alcohol (5 grams), for 10 hours at 140°. The oily product is heated with strong hydrochloric acid at 125—130°, and distilled with potash. The *aurochloride*, $C_{17}H_{17}N,HAuCl_4$, crystallises from dilute hydrochloric acid in flat, yellow needles, which melt at 100°. N. H. M.

Dipiperidyl and Dipicolyl. By F. B. Ahrens (*Ber.*, **21**, 2929—2932).—*Dipiperidyl* is obtained when γ-dipyridyl is reduced with sodium and alcohol and the product purified by means of the nitroso-derivative. It crystallises in colourless needles, melts at 120—122° with previous softening, and is readily soluble in alcohol and ether, but insoluble in water. It absorbs carbonic anhydride when exposed to the air, and is only slightly volatile with steam. The *platinochloride*, $C_{10}H_{20}N_2,H_2PtCl_6$, forms microscopic crystals, is only sparingly soluble in water, and blackens when heated at 195°. The *aurochloride*, $C_{10}H_{20}N_2,HAuCl_4$, crystallises in small, yellow needles, is readily soluble in hot, dilute hydrochloric acid, and is gradually decomposed when heated at about 160°. The *picrate* crystallises from hot water in needles; it blackens when heated, and is completely decomposed at about 257°. Mercuric chloride, phosphomolybdic acid, and potassium ferrocyanide produce precipitates in a solution of the hydrochloride.

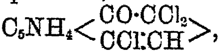
Dipicolyl, $C_{12}H_{12}N_2$, is obtained when picoline, boiling at 128—134°, is treated with sodium at 80—90°. After washing the product with water, it is dissolved in ether, the solution filtered, and the base extracted with dilute hydrochloric acid. The extract is mixed with excess of soda, the treatment with ether and hydrochloric acid repeated several times, and finally the ethereal solution is dried over potash and evaporated. The residual yellow oil is then distilled, and the portion passing at 270—300° collected; this distillate solidifies to a mass of yellowish, very deliquescent needles. The *platinochloride*, $C_{12}H_{12}N_2,H_2PtCl_6$, crystallises in small plates, and is very sparingly soluble in water, but readily in hydrochloric acid; it is only partially decomposed when heated at 275°. The *aurochloride*,

$C_{12}H_{12}N_2,HAuCl_4$, separates from warm, concentrated hydrochloric acid, in which it is readily soluble, in nodular crystals mixed with metallic gold; it is completely decomposed when heated at 200—201°. The *picrate* forms yellow, moss-like crystals, and is readily soluble in hot water. An aqueous solution of the hydrochloride gives precipitates with mercuric chloride, phosphomolybdic acid, potassium iodide, and potassium ferrocyanide. F. S. K.

Action of Chlorine on Hydroxyquinoline. By H. HEBEBRAND (*Ber.*, **21**, 2977—2989).—*Chlorhydroxyquinoline*, C_9NH_6OCl, is formed in small quantities when chlorine is passed into a well-cooled solution of 1-hydroxyquinoline (5 grams) in glacial acetic acid. Dichlorhydroxyquinoline (see below) separates at first, and is further converted into the hydrochloride whilst a further portion of the hydroxyquinoline is oxidised to the monochloro-derivative. As soon as the whole of the hydroxyquinoline is changed, the solution is filtered and the residue treated with absolute alcohol to dissolve the dichlorhydroxy-salt. The residue is dissolved in hot, dilute hydrochloric acid, the solution mixed with excess of sodium carbonate, and the precipitated monochlorhydroxy-compound recrystallised from methyl alcohol and light petroleum. It is thus obtained in colourless needles melting at 129—130°. The *hydrochloride* crystallises in small, yellow needles, melts at 253°, and is moderately soluble in alcohol and hot, dilute hydrochloric acid; it is very stable and sublimes in compact crystals. The *platinochloride*, $(C_9NH_6OCl)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles, and is readily soluble in hot but only sparingly in cold, dilute hydrochloric acid.

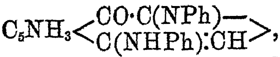
Dichlorhydroxyquinoline, $C_9NH_4Cl_2{\cdot}OH$ [$OH : Cl_2 = 1 : 2 : 4$], is prepared by passing chlorine into a 10 per cent. glacial acetic acid solution of hydroxyquinoline until the colour changes to yellow, pouring the solution into water, and recrystallising the precipitated product from alcohol. It is also obtained when trichloroketoquinoline (see below) is treated with hydrogen sodium sulphite or boiled with alcohol or dilute acids. It crystallises in long, slender needles, melts at 179—180°, and is readily soluble in warm alcohol or glacial acetic acid, but only moderately in hot benzene and light petroleum. It dissolves readily in alkalis and acids, forming yellow solutions, but the salts are unstable and cannot be recrystallised, and acid solutions are precipitated by water. When treated with chlorine in chloroform solution, it is converted into trichloroketoquinoline. The *hydrochloride* crystallises in long, yellow needles, and in aqueous solution gives a black precipitate with ferric chloride. The *platinochloride*, $(C_9NH_5OCl_2)_2,H_2PtCl_6 + 2H_2O$, crystallises in long, orange needles, and loses its water at 120°. The *acetyl*-derivative, $C_9NH_4OCl_2Ac$, separates from light petroleum in small, colourless crystals melting at 97—98°; it is very unstable, and is decomposed by water or when boiled for a long time with glacial acetic acid.

Trichlorhydroxyquinoline, [$OH : Cl_3 = 1 : 2 : 3 : 4$], is formed when the mother-liquor from trichloroketoquinoline is boiled or when the hydrochloric acid solution of pentachloroketoquinoline is treated with hydrogen sodium sulphite or with water. It crystallises from glacial acetic acid in long, colourless, moss-like needles, melts at 213—214°, and is readily soluble in hot alcohol or glacial acetic acid, but only sparingly in the cold solvents and in dilute acids; it is readily soluble in concentrated acids, but is reprecipitated on adding water. When treated with chlorine in chloroform solution, it yields a yellow powder, probably tetrachloroketoquinoline, which melts at 175° with decomposition, and is reconverted into trichlorhydroxyquinoline when boiled with alcohol. When heated with sodium carbonate, it yields a *sodium*-derivative melting at 270°. The *potassium*-derivative is crystalline. The *hydrochloride* crystallises in small, yellow needles. The *platinochloride*, $(C_9NH_4Cl_3O)_2,H_2PtCl_6 + 2H_2O$, crystallises from dilute hydrochloric acid in long, orange needles and loses its water at 140—150°. The *acetyl*-derivative separates from a mixture of glacial acetic acid and acetic anhydride in thin, transparent, forked, efflorescent crystals, melts at 172—173°, and is readily decomposed.

Trichloroketoquinoline hydrochloride, $C_9NH_4OCl_3,HCl + 2H_2O$, prepared by saturating a well-cooled glacial acetic acid solution of hydroxyquinoline with chlorine and washing the product with glacial acetic acid, is very unstable, hygroscopic, and sensitive to light. When simply dried between blotting paper, it melts at 93—95° to a yellow liquid which decomposes at 100—120° with evolution of gas and then solidifies, melting again at 170—180° with decomposition. When dried over sulphuric acid under reduced pressure, it does not begin to decompose until heated at 160° and melts at 180°. It is readily soluble in moderately dilute hydrochloric acid, but when the solution is evaporated under reduced pressure dichlorhydroxyquinoline separates. It is decomposed when warmed with solvents, generally with formation of the dichlorhydroxy-derivative, and this substance is formed very readily when the keto-derivative is reduced with hydrogen sodium sulphite. The *platinochloride* is very readily soluble, and when the solution is boiled or evaporated under reduced pressure, a mixture of platinochlorides is obtained. The free *base*,  $C_5NH_4{<}\begin{matrix}CO\cdot CCl_2\\ CCl{:}CH\end{matrix}{>}$, obtained by decomposing the hydrochloride with water and extracting the precipitated oil with ether, crystallises in long, thin, yellow prisms or needles, melts at 98°, turns brown at 130°, and is completely decomposed at 170°. It is readily soluble in benzene, alcohol, and glacial acetic acid, and does not decompose when kept.

Ethoxydichlorhydroxyquinoline, $OEt\cdot C_9NH_3Cl_2\cdot OH$ [$OH : Cl_2 : OEt = 1 : 2 : 4 : 1'$], is formed, together with dichlorhydroxyquinoline and a small quantity of the trichloro-derivative, when an alcoholic solution of freshly prepared trichloroketoquinoline is boiled for 1—2 hours. It crystallises from alcohol or benzene in long, thin, colourless needles, melts at 150—151°, and dissolves sparingly in most ordinary solvents in the cold but readily on warming. It is soluble in acids, forming colourless solutions, from which it is reprecipitated by water, and when warmed with alcoholic soda, it yields a solution from which a spongy sodium-derivative separates on cooling.

Dihydroxydichloroquinoline, [$(OH)_2 : Cl_2 = 1 : 1' : 2 : 4$], is obtained, together with ethyl chloride, when the preceding compound is heated at 110—120° with concentrated hydrochloric acid; it is also formed when trichloroketoquinoline is boiled with methyl alcohol. It crystallises from alcohol in needles, melts at 278°, and is more sparingly soluble than the chloro-derivatives of hydroxyquinoline. It crystallises from methyl alcohol in efflorescent needles containing alcohol.

Anilidoquinolinequinoneanilide,  $C_5NH_3<\begin{matrix}CO{\cdot}C(NPh)—\\C(NHPh){:}CH\end{matrix}>$, is obtained by treating an alcoholic solution of the ketochloro-derivative with excess of aniline. It crystallises in small, golden plates or long needles, melts at 222°, and shows all the properties of a feeble base. It is moderately soluble in glacial acetic acid, sparingly in alcohol, insoluble in water, and dissolves in dilute acids with a bluish-violet coloration. It is not changed by boiling with alcohol or concentrated potash, but is readily decomposed when heated with acids, yielding a yellow, crystalline substance which was not obtained in the pure state. The *hydrochloride* crystallises from acidified alcohol in small, dark-golden needles and is unstable. The *picrate* crystallises from alcohol in dark, copper-red needles. The *acetate* crystallises in needles, melts at 199°, and is decomposed by water.

Pentachloroketoquinoline platinochloride, $(C_9NH_3Cl_5O)_2,H_2PtCl_6$, is formed when trichloroketoquinoline hydrochloride (5 grams) is heated at 140—150° for six hours with manganese dioxide (35 grams) and concentrated hydrochloric acid (18 grams), the resulting solution filtered and mixed with platinic chloride. It is a yellow, crystalline compound, and when recrystallised or dried, it seems to lose hydrogen chloride and be converted into the salt of tetrachloroketoquinoline. A solution of pentachloroketoquinoline hydrochloride yields trichlorhydroxyquinoline when mixed with water or hydrogen sodium sulphite.

F. S. K.

Alkaloïds from Papaveraceæ. By E. SCHMIDT (*Arch. Pharm.* [3], **26**, 622—623).—The following abstract is the first of a series on these alkaloïds, giving the results of investigations undertaken at the instance of the author. Schiel's conclusion that chelerythrine and sanguinarine are identical is not confirmed. The former appears to have the formula $C_{19}H_{17}NO_4$, as deduced from the analysis of the small quantities obtained, whilst the latter, from the analysis of various compounds, has the formula, $C_{17}H_{15}NO_4$, thus confirming Naschold's result. Three more bases have recently been separated from *Chelidonium majus* which are now the subject of research.

J. T.

Chelidonine. By A. HENSCHKE (*Arch. Pharm.* [3], **26**, 624—644; compare Abstr., 1887, 854).—The alkaloïd was obtained partly by recrystallisation of the commercial base, and partly by direct extraction from the root of *Chelidonium majus*. Probst's method of extraction was employed, the stamped root being boiled in water acidified with sulphuric acid, ammonia in excess added, and the filtrate dried. This was purified by treatment with acidified alcohol, and again with ether, and finally was repeatedly crystallised from boiling alcohol. Chelidonine, $C_{20}H_{19}NO_5 + H_2O$, forms vitreous, tabular, colourless, monoclinic crystals of about 3 mm. diameter. The reactions of the base are given in detail. Solutions of the salts of this base have an acid reaction, and the hydrochloride has the formula $C_{20}H_{19}NO_5\cdot HCl$; the nitrate, $C_{20}H_{19}NO_5,HNO_3$; the sulphate, $C_{20}H_{19}NO_5,H_2SO_4 + 2H_2O$; the platinochloride, $(C_{20}H_{19}NO_5)_2,H_2PtCl_6 + 2H_2O$; this was not obtainable in a crystalline form; the aurochloride, $C_{20}H_{19}NO_5,HAuCl_4$, is easily obtained in crystals. Ethyl iodide combines with the base, and the compound is not acted on by potassium hydroxide; these and less positive results lead to the conclusion that chelidonine is a tertiary base. By oxidation with potassium permanganate in alkaline solution, chelidonine yields oxalic acid, methylamine and ammonia, the latter resulting from the decomposition of methylamine. In acid solution, the oxidation goes further, carbonic anhydride and methylamine resulting. J. T.

Alkaloïds from Cod-liver Oil. By A. GAUTIER and L. MOURGUES (*Compt. rend.*, **107**, 626—629; compare Abstr., 1888, 1315).—*Aselline*, $C_{25}H_{32}N_4$, is an amorphous, colourless solid which becomes green on exposure to light. It melts to a viscous, yellowish liquid with an aromatic odour recalling that of the ptomaïnes, is very slightly soluble in water, to which it imparts a bitter taste and an alkaline reaction, but dissolves in ether and still more readily in alcohol; sp. gr. about 1·05. The salts of aselline crystallise readily, but are partially decomposed by water. The mercurochloride crystallises from warm water; the aurochloride is very easily reduced; the platinochloride is orange-yellow, and dissolves in warm water, but is decomposed by boiling water. Aselline is feebly toxic, and produces fatigue and stupor; 3 mgrms. of the hydrochloride killed a greenfinch in 14 minutes.

Morrhuine, $C_{19}H_{27}N_3$, is separated from aselline by taking advantage of the greater solubility of its platinochloride. It is a thick, oily, amber-coloured liquid with an odour which recalls that of aselline, and is only slightly soluble in water, but more soluble in alcohol and ether. It is caustic and strongly alkaline, and absorbs carbonic anhydride from the air. The hydrochloride is very deliquescent; the aurochloride is yellow, and dissolves in warm water; the platinochloride is somewhat soluble and crystallises in needles.

Morrhuine constitutes one-third of the total bases in the oil, and an ordinary dose of one fluid ounce contains 2 milligrams. It excites the appetite and has remarkable diaphoretic and diuretic properties. In large doses it produces fatigue and stupor. C. H. B.

Physiological Chemistry.

The Nature of Fibrin Ferment. By W. D. HALLIBURTON (*J. Physiol.*, 9, 227—286).—This paper gives a full account of the researches of which a preliminary account has already been published (Abstr., 1888, 974). W. D. H.

The Glycogen in Muscle after Section of its Nerve and its Tendon. By E. KRAUSS (*Virchow's Archiv*, **113**, 315—332).—The first part of this paper is devoted to the histological changes that occur in muscle after neurotomy and tenotomy respectively.

For the glycogen estimations, the tendo Achillis was divided in 21 rabbits, and the sciatic nerve in 16 others. The animals were then fed for 1 to 3 days before death with 15—30 grams of sugar dissolved in water. The glycogen was determined by Külz' method (Abstr., 1886, 494). The animals were killed at different periods varying from 2 to 124 days after the operation.

The results of analysis, given in tabular form, show after neurotomy an increase of glycogen in 8, a normal amount in 3, and a decrease in 4 cases; after tenotomy an increase in 6, a normal amount in 8, and a decrease in 2 cases. The general result is therefore that in the pathological condition of muscle produced by section of its nerve or of its tendon, metabolism is altered in such a way that glycogen is not got rid of so easily as in healthy muscle. W. D. H.

Lactic Acid in the Blood. By G. SALOMON (*Virchow's Archiv*, **113**, 356—360).—Gaglio (*Arch. Anat. Physiol.*, *Phys. Abth.*, 1886, 400), and Berlinerblau (Abstr., 1888, 974) have described lactic acid as a constituent of blood. The author has for some years made similar observations in cases of disease. Thus in a specimen of leucæmic blood he found 0·05—0·06 per cent. of lactic acid; in pleural exudation from a case of carcinoma, there was a percentage of 0·007. In both cases, estimation of the water of crystallisation, and of the zinc in the zinc salt showed that sarcolactic acid was the particular form of lactic acid that was present.

More extended observations, however, have shown that lactic acid in the blood is not characteristic of the diseases mentioned, but can be obtained from the blood of patients who have died from nearly every variety of disease. Observations on the blood removed from the vessels during life show, however, that lactic acid is then as constantly absent as it is present in the blood examined after death.

If the blood is examined immediately it is drawn, lactic acid is found to be absent, but if the blood is allowed to stand a short time and then examined, the acid will then be found. Its formation is connected with the ferment actions that set in in shed blood, or in blood left in contact with dead tissues. If it is formed at all during life, it must be rapidly oxidised, and so cannot be discovered in living blood. W. D. H.

Micro-organisms and Proteolytic Digestion. By V. D. HARRIS and H. H. TOOTH (*J. Physiol.*, 9, 220—226).—The experiments of which this is a preliminary account gave the following results:—

(1.) The general belief that micro-organisms need take no part in gastric digestion, and are generally absent was confirmed.

(2.) Experiments to prove that micro-organisms are themselves competent to convert proteïds into peptone were very unsatisfactory; albumoses have been noticed, but never true peptone. Perhaps some special micro-organism is necessary.

(3.) As it was found exceedingly difficult to exclude micro-organisms in pancreatic digestions by employing strictly the principles of Listerian surgery in the removal of the pancreas, the organisms were killed by the addition of antiseptic reagents, of which mercuric chloride and phenol were found to be the most effective. It was found that the tryptic ferment is able to convert proteïds into peptone without the aid of micro-organisms, although that is no proof that the micro-organisms do not assist in the action in the intestine. Phenol, however, either prevents the pancreatic ferment from forming leucine and tyrosine, or else the formation of these substances depends in part at all events on bacteria.

(4.) With regard to the production of indole, it was found that the appearance of indole and its allies in alkaline pancreatic fluids is very capricious and can be easily prevented. In plugged flasks, it may not appear for a considerable time, no other precaution being taken than that of simply plugging the flasks, micro-organisms being present in large numbers. The smallest amount of mercuric chloride or phenol, even if not sufficient to render the liquid aseptic, also prevents the formation of these substances. Indole appears most readily in the digestion of uncoagulated (unboiled) proteïds. Whenever it is present, large numbers of all sorts of bacteria are there also, still it may be absent even if swarms of micro-organisms are present. It thus appears that there are special indole-forming organisms. Experiments with pure cultivations of the different forms of bacteria found are, however, at present incomplete. As a result of inoculation of solutions of pure peptone, and of solutions of leucine and tyrosine with a mixture of bacteria potent to cause the formation of indole, it was found that indole is formed from the peptone, not from leucine or tyrosine. It seems, therefore, likely that the formation of indole and its allies in the alimentary canal below the stomach is an alternative course for the excretion of nitrogen to that by the formation of leucine and tyrosine. W. D. H.

Glycogen in Diabetic Urine. By W. Leube (*Virchow's Archiv*, **113**, 391—393).—E. Reichardt (*Zeit. anal. Chem.*, 1875) has described "dextrin" as occurring in diabetic urine. Glycogen has, however, never been detected before. Two cases were examined in the present research. A large amount of urine (3—5 litres) was precipitated with alcohol, the precipitate collected and washed free from sugar. The precipitate was then dissolved in water, and the solution gave a brown colour with iodine; on boiling the solution with 10 per cent. of sulphuric acid, the carbohydrate (probably glycogen) was converted into dextrose. In one of the two cases, the amount of glycogen present was very small. It is considered probable that the sugar in the blood is partly converted into glycogen as it passes through the epithelium of the urinary tubules. W. D. H.

Aromatic Substances in Febrile Urine. By J. S. Haldane (*J. Physiol.*, **9**, 213—219).—Diseases and conditions of the body where putrefactive changes are greater than normal, cause the appearance of an increased quantity of certain aromatic substances, phenol, cresol, indole, scatole, &c., in the urine.

Brieger (*Zeit. klin. Med.*, 3, 465) classes, however, scarlet fever and diphtheria as putrefactive diseases with erysipelas and pyæmia in which putrefactive processes no doubt often go on. It seemed advisable therefore to repeat these observations with regard to scarlet fever and diphtheria, especially as Brieger's method, which consisted in weighing the phenol as tribromophenol, was found to be wanting in accuracy. It was found that the more concentrated the urine, the greater was the quantity of tribromophenol obtainable from it, on account of the solubility of the bromine-water precipitate. In fact, on comparing Brieger's results with control experiments performed with a urine concentrated to different extents, it was found that the increase in phenol as described by Brieger in scarlet fever and diphtheria, could be equally well explained by the rise of the specific gravity of the urine in those diseases. The method adopted was therefore that of estimating the proportion of sulphuric acid combined as ethereal hydrogen sulphates to that combined as ordinary sulphates. Taking the normal proportion as 1 to 10, it was found in 16 cases of scarlet fever in which the urine was passed during the fever to be 1 to 17, and in 13 cases in which the urine was passed during the first three days of convalescence to be 1 to 21: so far as the chemical composition of the urine goes, there is thus no ground for regarding scarlet fever as analogous to a putrefactive process.

The average of the ratio in five analyses made in cases of diphtheria was 1 to 13, hence in these cases also there was no increase in the elimination of aromatic substances. W. D. H.

Physiological Action of Para- and Meta-phenylenediamine. By R. Dubois and L. Vignon (*Compt. rend.*, **107**, 533—535).—Meta- and para-phenylenediamines are similar in constitution to the ptomaïnes and leucomaïnes, and their physiological action is therefore of considerable interest.

In doses of 0·1 gram per kilo. of body-weight, both compounds produce salivation, vomiting, diarrhœa, excessive emission of urine, and coma. Death follows in two to three hours in the case of the para-derivative and in 15 hours with the meta-derivative. The compounds remove oxygen from the blood and tissues in the same way as micro-organisms which are rapidly multiplying, and the brownish products thus formed impart a dark colour to the blood and tissues.

Metaphenylenediamine produces in the dog all the symptoms of aggravated influenza, with continual sneezing and a hoarse cough, which ends in coma and death. Paraphenylenediamine produces very remarkable exophthalmia, the tissues of the eye undergoing complete alteration. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Action of Micro-organisms on certain Colouring Matters. By J. RAULIN (*Compt. rend.*, **107**, 445—447).—*Aspergillus niger* will grow in cultivation liquids containing ammonium nitrate, but not in similar liquids containing salts of aniline, rosaniline or indigocarmine.

Slightly acidified yeast solution, beer wort, and sugar solution tinted with indigocarmine, slowly decolorise in presence of air and in absence of all organisms, but this change is due to oxidation and does not take place in an atmosphere of carbonic anhydride. Certain aërobic organisms retard or prevent decolorisation by preventing the access of oxygen.

Active beer-yeast also decolorises indigocarmine in absence of oxygen, but decolorisation is due to reduction and the colour returns if the liquid is exposed to air. In this case, reduction is accompanied by the development of micro-organisms similar in appearance to the lactic ferment. The change takes place most rapidly if the yeast solution has been exposed to the air at 24° for several days; it then acquires a putrid odour and is full of bacteria. The rate of decolorisation increases with an increase in the number of organisms, and the addition of an antiseptic, or any other cause which destroys the organisms, prevents the changes. Reduction is due to changes connected with the vital processes of the organisms, and is not due to the liberation of hydrogen. It is not analogous to the reduction of indigocarmine by an alkaline solution of glucose, since in that case the presence of organisms is not essential.

Similar reducing actions were observed with logwood, orchil, cochineal, safranin, and several artificial colouring matters.

C. H. B,

Decolorisation of Tincture of Turnesole in closed Vessels. By R. DUBOIS (*Bull. Soc. Chem.*, **49**, 963—964).—The decolorisation of turnesole kept in a closed vessel is entirely due to the action of germs, as when the solution is sterilised the blue colour is permanent. The colourless solution contains only one species of living organisms; this is a very small, completely spherical micrococcus, which can be cultivated in slightly alkaline peptonised gelatin. The liquid decolorised by these micro-organisms at once regains its blue colour on exposure to the air. F. S. K.

Formation of Starch from Various Substances. By T. BOKORNY (*Chem. Centr.*, 1888, 858—859, from *Ber. deut. bot. Ges.*, **6**, 116—120).—Since earlier experiments had proved that algæ can be fed with methylal, the author has shown, by means of further experiments, that starch is formed from methylal. Spirogyra were used as the material for the investigation. Whilst in the absence of light, the formation of starch could not be observed, its formation could be readily detected after the spirogyra had lain in 1—0·1 per cent.

methylal in the sunlight. Spirogyra fed on solution of methyl alcohol of the same strength, namely, 1—0·1 per cent., showed at the end of 6 to 24 hours a very considerable new formation of starch. The author finds that glycol and glycerol, like mannitol, are also able to form starch. J. W. L.

Matter Excreted by Roots. By H. Molisch (*Ann. Agronom.*, **14**, 334—335).—It is known that roots excrete an acid juice capable of attacking minerals. The author finds that the liquid has much more extensive powers, namely, it has both reducing and oxidising properties; turns tincture of guaiacum blue; oxidises tannins and humic substances, and consequently promotes the decomposition of humus: transforms cane-sugar into reducing sugar, and acts feebly like diastase; corrodes a plate of ivory; and modifies the organic matter of soil. The root membranes are not simply permeated with this juice, it may sometimes be seen to exude in droplets.

J. M. H. M.

Occurrence of Solid Hydrocarbons in the Vegetable Kingdom. By H. Gutzeit (*Ber.*, **21**, 2881—2882. Compare Abbot and Trimble, Abstr., 1888, 1329).—The author points out that he has already described solid hydrocarbons which were obtained from the fruit of *Heracleum giganteum hort.*, *Heracleum spondylium*, L., and *Pastinaca sativa*, L. (*Beiträge zur Pflanzenchemie*, Jena, 1879), and that others have already proved the presence of such compounds in the vegetable kingdom. F. S. K.

Constituents of Bark of Rhamnus Frangula and R. Purshiana. By P. Schwabe (*Arch. Pharm.* [3], **26**, 569—594).—The coarsely powdered bark is freed from fat by means of ether, and extracted with 98 per cent. alcohol; the extract is mixed with several times its volume of water, and is shaken up by portions with ether. The first ethereal solutions are dark coloured, but on repeating the operation 10 or 12 times the ether remains colourless. The united ethereal solutions are distilled, when a light-yellow deposit forms in thin layers on the side of the vessel. The deeply coloured mother-liquor is filtered after remaining 24 hours. The residue on the filter is repeatedly washed with alcohol and ether, and finally crystallised several times from boiling alcohol, until the microscope shows distinct crystallisation, undoubtedly due to frangulin. The mother-liquor filtered from frangulin was brought to dryness, taken up with a little alcohol, mixed with several times its weight of water and again shaken up with ether, but only once or twice; in this way the beautifully crystalline body emodin (trihydroxymethylanthraquinone) was separated. On distilling off the ether, the residue is readily seen under a lens to be permeated with crystals. This is heated with glacial acetic acid, in which it readily dissolves, and on cooling emodin crystallises out. Recrystallisation yields emodin as a light red crystalline mass, which melts at 254°. The yield was frangulin 0·06 per cent., and emodin 0·10 per cent. Fresh bark gave no frangulin, thus confirming an observation previously made by Casselmann; whilst bark a year and a-half old gave frangulin 0·04 per cent., and emodin 0·10 per cent. as before. *Emodin*, $C_{15}H_{10}O_5 + H_2O$, gives red to brown-red amorphous precipitates with the alkaline earths and with lead, copper, and mercury salts. It dissolves in dilute alkalis to a splendid dark cherry-red colour, but gives no crystals on evaporation. A solution in alcoholic potash, heated at 100° in a sealed glass tube, showed fine needle-like aggregates after standing unopened for 24 hours. *Frangulin* melts at 228° to 230°, whilst Casselmann puts it at 249° and Faust at 226°, the differences being due to impurity in the last two cases. It is almost insoluble in water and ether, more easily in chloroform, benzene, and alcohol, and very soluble in hot acetic acid. When dry, it forms a beautiful, light-yellow, brittle mass, with somewhat silky lustre. Its composition is $C_{21}H_{20}O_9$. Four to five hours' boiling with 20 per cent. sulphuric acid converts it into emodin and glucose. If anywhere, frangulinic acid should make its appearance here, but the compound previously described under this name is identical with emodin.

The coarsely powdered root of *Rhamnus purshiana* (*Cascara sagrada*) was extracted with ether, and then with 98 per cent. alcohol. After the addition of water, the ether extract was shaken repeatedly with light petroleum until the oily extracts became almost colourless. On removing the petroleum, the dark-coloured mother-liquor gave an immediate brown-red, flocculo-crystalline precipitate. As in the case of *Rhamnus frangula* bark, the alcoholic extract shaken up with ether after the addition of water afforded a crystalline product. The petroleum product which proved to be identical with this, was found to be emodin. Frangulin was not present, although it may possibly occur in older bark. J. T.

Japanese Tobaccos. By M. Fesca and H. Imai (*Bied. Centr.*, 1888, 629—637).—The authors analysed the soils and the tobaccos produced in a locality in Oyamada, and also one other Japanese tobacco. Permeability and a certain amount of humus are far more important as regards the soil than the amount of plant food, as the latter can be supplied by manuring. The best tobacco soil exhibited only a moderate absorptive power for bases. The manures applied are human and animal excreta, wood and straw ashes, and bath-water. As regards analysis as a means of judging the quality of a tobacco, the authors came to the following conclusions:—(1.) Just as an alcoholic drink should contain a certain percentage of alcohol, so a tobacco should contain a certain percentage of nicotine; but that the quality of a tobacco depends on the percentage of the nicotine has not yet been proved. (2.) Nitric acid is not contained in well-fermented tobaccos. (3.) The ammonia in the older analyses was too high, as it included some that came from amides. The ammonia, which only comes to some tenths of a per cent., cannot account for lowered quality. (4.) The amount of albuminoïds, reckoned as it formerly was, without allowing for the amide-nitrogen present, affords no standard for judging tobacco. The worst tobacco analysed had the lowest total nitrogen, yet owing to the nicotine and amides being very low, it had the highest amount of albuminoïds. (5.) Amide nitrogen for the most part indicates the presence of compounds which do not injure and perhaps even enhance the quality of the tobacco. One of the most important duties of the fermentation is to change albuminoïds into amides. (6.) The determination of the amount of substances that ether extracts is of but little use. (7.) Carbohydrates, with the exception of cellulose, should not be present in well-fermented tobacco. A study of their decomposition, and of the formation and decomposition of organic acids and of amides should prove useful in determining the quality and guiding the culture and treatment of tobacco. (8.) Distinctions as to quality can only be drawn when the differences in the amounts of the substances estimated are considerable, and they can only be made safely when the whole composition proves quite satisfactory or quite the reverse; they can rarely be drawn from differences in the amounts of single substances. Inferiority can be more safely inferred than superiority. In very bad tobacco, the albuminoïds, the sulphuric acid, the chlorine and generally the mineral acids are high, whilst the amide nitrogen and the potash are low.

The remaining conclusions relate to the ash constituents. (9.) To indicate good quality and especially combustibility, there should be a medium amount of bases, especially of potash and lime. Within certain limits these bases appear capable of replacing one another. The percentage of one or the other must fall very low before it is to be regarded as a bad indication. Magnesia, if exceptionally high, appears to injure the combustibility. (10.) Mineral acids if high indicate bad combustibility; but they must be exceptionally high to surely indicate low value. Apart from silica, phosphoric acid appears to be the least injurious, chlorine considerably more, and sulphuric acid the most injurious to the quality and combustibility. (11.) The bases soluble in water and either free or existing as carbonates, appear to have no important influence, but the amount of carbonic anhydride up to a certain point indicates increased combustibility, and a large amount of carbonates in proportion to mineral salts indicates good value. (12.) A high proportion of bases in the ash, provided it is not caused by magnesia or iron, points especially to good combustibility.

H. H. R.

Formation of Nitrates in Soils of different Degrees of Fertility. By P. P. DEHÉRAIN (*Ann. Agronom.*, **14**, 289—320).—It appears probable, from the researches of Lawes and Gilbert, Warington, and others, that a soil exhausted by cropping contains only nitrogenous organic matter difficult to nitrify, and that the relative sterility which is produced by a number of successive crops without manure, is due not only to a decrease in the total amount of nitrogen, but also to the residual nitrogenous matter being less apt to nitrify than that in a fertile soil. To obtain confirmation of this, the author has studied the rate of nitrification in different soils, fertile and exhausted, manured and unmanured, under different conditions of humidity, temperature, division, &c. A few only of the results, most of which are provisional and require further elucidation, are given below. A saturated atmosphere is ultimately unfavourable to nitrification; probably because moulds are encouraged which destroy the nitrate. Soil very finely sifted, placed in a funnel, and submitted to frequent waterings, so as to alternate periods of comparative dryness and moisture, is very favourably circumstanced for nitrification; for example, in the 189 days from 17th May to 22nd November, there was formed per 1000 kilos. of soil, 880 grams nitric acid: reckoning the weight of the soil at 3600 tonnes per hectare, this would give 819·8 kilos. nitrogen per hectare nitrified in that space of time, a quantity infinitely superior to the requirements of the most exhausting crop. The waterings in this experiment were equivalent to five times the normal rainfall. The accumulation of nitrate in the soil, at any rate to the extent of 700 mgrms. per kilo., does not retard the rate of nitrification. The organic matter was more nitrifiable at the commencement of the experiment than afterwards, since much more nitrate was formed in the first 27 days than in any subsequent similar period, notwithstanding the lower temperature of this first month as compared with the two following. Again, in the December to January period more nitrogen was nitrified per diem than in the October to November period, in spite of the lower temperature; from this the author infers that the organic matter of the soil is subject from time to time to changes rendering it more or less easy of nitrification. Trituration of the soil and elevation of temperature were both found to greatly accelerate nitrification. The addition of sodium nitrate to the soil in quantities of 0·06 and 0·60 per cent. almost prevented nitrification for the first 40 days, and greatly retarded it during a subsequent like period, although eventually nitrification at something like the normal rate occurred; the addition of 1 : 1000 of common salt to the soil exercises little or no effect, 2·5 : 1000 is injurious, and 5 : 1000 prevents nitrification.

Three soils, long unmanured and poor in nitrogen, developed very little nitrate for some weeks after being placed in circumstances the most favourable for nitrification, but afterwards fairly rapid nitrification set in, which the author attributes to changes undergone by the organic matter under the new conditions. A fourth poor soil, unmanured and equally poor in nitrogen with the other three, proved, however, very nitrifiable, it developed from the first more nitrate than a fertile soil placed in the same conditions. J. M. H. M.

Loss and Gain of Nitrogen in Agriculture. By B. FRANK (*Bied. Centr.*, 1888, 610—617).—Among the sources of loss is the volatilisation of ammonia from the soil. In some experiments in which ammonium sulphate solution was added to samples of soil, the author found that the ammonia thus added soon disappeared, being to a small extent converted into nitrates whilst the greater part volatilised. A light and pure sandy soil does not expel the ammonia and has only a feeble nitrifying power, so that the ammonium salt is retained nearly undiminished for a long time. Of the individual constituents, quartz grains and clay are inactive, whilst calcium carbonate causes both slow nitrification and also partial liberation of ammonia. Another source of loss was mentioned by Boussingault, namely, that when nitrates were given to plants growing in the dark, there was a liberation of free nitrogen, which he attributed to the action of some organic substance excreted by the roots. The author experimented on the point, growing bean seeds in the dark in nutritive solutions, both with and without nitrogen compounds. As in every case there was a loss of nitrogen, it could not be due to reduction of nitrates, and he attributes it to the loss of nitrogen consequent on the decay of those parts of the seed not made use of by the germinating plant.

Next, treating of the gain of nitrogen, he combats Hellriegel's view that the root nodules of the Leguminosæ are concerned in rendering free nitrogen available to the plant. His own experiments lead him to the conclusion that the land gains in combined nitrogen in some way besides that caused by lightning discharges, which at present is the only one undisputed. He found that the presence of vegetation raised the amount of this gain, that this could not be accounted for by the ammonia of the air, and that it must be derived from the free nitrogen of the air. The gain rises with increased plant development, and both the kind of soil and the species of plant have an influence. Lupines are very effective as compared with non-leguminous plants; but the difference in the powers of increasing the combined nitrogen is one of degree, not one of kind; hence it cannot be ascribed to the nodules. Further, nodules did not occur in lupines grown in sterilised soil, yet the plants developed better than in a parallel experiment with unsterilised soil where the plants had nodules, and besides the nodules the legumes have no other organs to supply nitrogen which other plants do not also possess. The next question is how soil unoccupied by a crop gains in combined nitrogen. This gain takes the form chiefly or entirely of organic nitrogen compounds, thus agreeing with Berthelot's experiments, and is explained by the growth in the soil of the cryptogamic plants, algæ containing chlorophyll and allied forms which the author discovered there. He next discusses the question whether these plants avail themselves of free nitrogen or of nitrogen oxidised in the soil by an inorganic process. He asserts that under the influence of calcium or magnesium carbonates free nitrogen can be oxidised to nitric acid, the action being distinct at 100°, still apparent at 45—50°, and no longer apparent at 15—22°, but thinks that in the German climate this action can only very rarely occur. He concludes that it is not an inorganic process that makes the free nitrogen available, but that the combined nitrogen is due to a development of plant cells containing albuminoïds which is not to be connected with any process occurring in the soil. This power of assimilating free nitrogen is very different for different plants; the result is smallest in fallow land, where only the lower plant forms are at work; it is larger with higher plant forms, and among these the lupines and probably other Leguminosæ produce the greatest result.

H. H. R.

Action of Superphosphate on Nitrates. By A. DEVARDA (*Chem. Centr.*, 1888, 899—900).—Experiments by the author go to show that, at the ordinary temperature, the phosphoric acid, hydroflouric acid, and readily decomposable organic compounds, as well as ferrous salts present in superphosphates, cause no loss of nitrogen from nitrates which may have been mixed with them. In those cases, however, where the mixtures are exposed to a moderately high temperature, the loss of nitrogen is considerable, although in this

case the ferrous compounds take no part in the reaction. The author also found that in mixtures of superphosphate and nitrates the soluble phosphate becomes insoluble much more quickly than when the nitrate is omitted, and the mixing of nitrate with superphosphate for any length of time is therefore not to be recommended.
J. W. L.

Analytical Chemistry.

Preparation of Starch Solution for Use in Volumetric Analysis with Iodine. By G. Gastine (*Bull. Soc. Chim.*, **50**, 172—173).—Five grams of potato-starch is mixed with 0·01 gram of mercury iodide, stirred with a little water, and poured into boiling water (1 litre). It is allowed to settle, and the clear liquid poured off. A solution prepared in this manner has been kept for more than a year without deteriorating. N. H. M.

Use of Salicylic Acid for Preserving Standard Solutions. By H. Bornträger (*Zeit. anal. Chem.*, **27**, 641—642).—The addition of a pinch of salicylic acid to each litre of a thiosulphate solution greatly diminishes its tendency to decompose. The author's determinations show large variations, but not a progressive diminution in strength. M. J. S.

Applications of Spectrophotometry to Chemical Physiology. By E. Lambling (*Arch. de Physiol.*, 4th Series, **12**, 1—34).—This paper gives an historical account of the spectrophotometer, and of the principles upon which the spectrophotometric method depends. The practical application of the method for quantitative purposes involves:—(1) The choice of a region of the spectrum; (2) the determination of the coefficient of extinction of the coloured solution for that region; and (3) the determination of the amount of absorption of the colouring matter for the same region. When two colouring matters are mixed in a solution, they may also be estimated quantitatively, provided the absorptive power of each of the two pigments for two regions of the spectrum be previously known.

Finally, the application of such methods to animal pigments (of the blood, bile, urine, &c.), is pointed out. W. D. H.

Determination of Chlorine in Plant-ashes. By A. Jolles (*Chem. Centr.*, 1888, 863—864, from *Zeit. Nahrungsmittel u. Hygiene*, **2**, 81).—The method the author proposes as the best is as follows:—The plant (10 grams) is incinerated gently in a platinum dish, moistened with an alcoholic solution of sodium carbonate, the alcohol burned off, and the process repeated; after this, the whole of the carbon may be burnt off without any fear of chlorine being lost, and the ash may be extracted by means of water and the determination finished in the usual manner with silver nitrate. This deviation from the ordinary direct combustion of vegetable matter in the determination of chlorine obviates the chance of a loss of this element which might otherwise take place. J. W. L.

Method for the Determination of Bromine in Sea-water. By F. GUTZKOW (*Chem. News*, **58**, 190—193).—250 c.c. of sea-water is mixed with a drop or two of sulphuric acid and with 100 c.c. of a solution containing about 25 grams of copper sulphate. It is then treated with sodium sulphite solution until the precipitate redissolves with difficulty, and heated until the blue colour returns; more sodium sulphite is now added, about one-third that already used, and the whole again heated until blue, and then cooled. In this way, all the bromine is precipitated in a few minutes. After washing the precipitate, first with 100 c.c. of water containing 1 gram of sulphuric acid, then with a few drops of sodium carbonate solution, it is warmed with hydrochloric acid until all sulphurous anhydride is removed, and is finally treated with zinc. The filtrate and washings from the copper, which combined should not exceed 25 c.c., are titrated with sodium hypochlorite by a method of the author's which is described in detail in the original. The flask containing the liquid is fitted with a triple-bored cork; through one hole passes a tube closed by a piece of india-rubber tubing and a clip, through the other holes two thistle-headed funnels reaching nearly to the bottom of the flask, one is roughly graduated. By blowing into the tube, a quantity of liquid is forced up both funnels and is titrated in the graduated one, the other serving for comparing the colour; in this way an indication of the quantity of hypochlorite required by the whole liquid is obtained, and so the operation can be finished with greater rapidity than by the ordinary mode of procedure. D. A. L.

Determination of Fluorine in Substances Decomposable by Sulphuric Acid and especially in Natural Phosphates. By H. LASNE (*Bull. Soc. Chim.*, **50**, 167—170).—Sufficient substance to yield 0·2 gram of calcium fluoride is put into a flask containing strong sulphuric acid (50 c.c.) and pure sand (10 grams), and connected with two wash-bottles, the first of which contains 2·5 grams and the second 0·5 gram of soda dissolved respectively in 25 c.c. of water. Dry air is passed into the flask, which is heated for an hour at 180—200°; it is then allowed to cool, dry air being passed through. The soda solutions are united and boiled for ¼ hour; phenolphthaleïn is added, and carbonic anhydride passed through the solution until it is colourless; it is then heated for ½ hour at 50°, and treated with ammonium carbonate, when the silica is almost completely precipitated. The liquid is cooled quickly, diluted to 125 c.c., filtered through a large folded filter, and 100 c.c. collected. A few drops of tropæoline solution is added to the solution, which is carefully neutralised with dilute hydrochloric acid. It is then treated with pure sodium carbonate (equal to 0·5 gram of anhydrous carbonate), boiled until free from carbonic anhydride, and precipitated with a slight excess of calcium chloride. The precipitate is ignited, treated with acetic acid, evaporated to dryness, again treated with acetic acid, and the undissolved calcium fluoride, washed, ignited, and weighed. N. H. M.

General Method for the Separation and Volumetric Estimation of Acids: Application to Sulphuric Acid. By G. LINOSSIER (*Bull. Soc. Chim.*, **50**, 46—47).—The method is applicable to all acids which yield insoluble compounds when combined with metals which are precipitated by hydrogen sulphide in acid solution. The determination of sulphuric acid is carried out as follows:—The solution of the sulphate (containing 0·05 to 0·1 gram) contained in a dish is treated with alcohol (2 vols.), heated almost to boiling, and precipitated with a slight excess of lead acetate. When cold it is washed by decantation with a mixture of alcohol and water (0·5 to 1 vol.), passing the decanted liquid through a small filter. The trace of lead sulphate on the filter is washed with aqueous hydrogen sulphide into a flask; the rest of the lead sulphate is shaken with a saturated solution of hydrogen sulphide, the liquid poured on to a filter, and the precipitate treated with a fresh amount of hydrogen sulphide and filtered. It is then washed with aqueous hydrogen sulphide until the filtrate gives no reaction with Poirrier's orange. The whole of the sulphuric acid is then in the filtrate, and is titrated with decinormal soda solution. N. H. M.

Volumetric Estimation of Boric Acid, and of Ammonia in Ammonium Salts. By J. MCGLASHAN (*Chem. News*, **58**, 175—176).—By using Poirrier's oranges I and II, boric acid and ammonium borate can be titrated directly with normal soda, but borax must first be made neutral to methyl-orange with sulphuric acid; boracite must be heated with dilute sulphuric acid, made neutral to methyl-orange with soda, and any carbonic anhydride eliminated before titrating. Ammonia is objectionable in any form except as borate or hydroxide, the latter when dilute is neutral to both oranges. Therefore, with these indicators ammonia may be titrated with soda, in any ammonium salt, without distillation. With ammonium carbonate and with arsenates, the end reaction is not distinct, but with hydrogen sulphide it is sharp. D. A. L.

Resorcinol as a Test for Nitrates. By D. LINDO (*Chem. News*, **58**, 176—177).—For testing with resorcinol, 10 grams are dissolved in 100 c.c. of water, and one drop of this solution, one drop of 15 per cent. hydrochloric acid, and 2 c.c. of concentrated sulphuric acid are added to 0·5 c.c. of the nitrate solution (compare Abstr., 1888, 1337); one in 500,000 gives a definite permanent purple colour after some time, whilst with increasing strengths of nitrate solution the colour becomes more intense, until with one in 10,000 the vivid purple-red colour is so intense as only to be distinctly seen in the lower portion of the band. Resorcinol is valueless without hydrochloric acid, but with it, is a more delicate test for nitrates than ordinary phenol. Copper sulphate does not aid the reaction materially. The reagents alone gave a band which, however, cannot be mistaken for the nitrate band. With nitrites, it is more delicate than with nitrates; with chlorates it is no good, with dichromate (0·5 gram per litre) it gives a red to buff upper with a purplish lower band, the latter changing to pink or with hydrochloric acid to reddish-brown; the colours are slightly different if the acid is run in at once, or after some delay. Permanganate, N/10, with 4 vols. water, gives a dark-orange upper and yellowish lower band; with hydrochloric acid, these are respectively orange, red, and greenish. Hydrogen peroxide in dilute solution yields a green and brownish compound band. D. A. L.

Estimation of Phosphorus in Iron and Steel. By P. W. SHIMER (*Chem. News*, **58**, 165—166).—Dissolve 1 gram of iron in 20 c.c. of nitric acid, sp. gr. 1·20, and add to the boiling solution 10 c.c. of a solution of 20 grams of potassium permanganate in a litre of water, 2·5 c.c. at a time, and after a few minutes 5 c.c. of hydrochloric acid, sp. gr. 1·12. When the action has ceased, add a mixture of 5 c.c. of concentrated sulphuric acid and 5 c.c. of water, and evaporate until fumes of sulphuric acid begin to come off. When cool, add 5 c.c. of nitric acid, sp. gr. 1·20, and sufficient water; boil to dissolve iron salts, filter, and wash with water. The residue serves well for the estimation of silicon. Heat the filtrate to 80° and add 5 c.c. of ammonium molybdate (5 grams of MoO_3, 20 c.c. ammonia, sp. gr. 0·96, 30 c.c. nitric acid, sp. gr. 1·20), then keep at 60° until the liquid is clear, which occupies less than an hour when the solution is not too dilute. The yellow precipitate is washed with acid ammonium nitrate solution, dissolved in ammonia and precipitated by magnesia mixture. The method gives good results both for silicon and phosphorus.

A few experiments were made using sulphuric acid and ammonium sulphate instead of nitric acid and ammonium nitrate for the molybdate precipitation, with satisfactory results. D. A. L.

Influence of Sulphur on Eggertz's Carbon Colour-test. By T. W. HOGG (*Chem. News*, **58**, 175).—When ordinary steels containing say 0·05 per cent. of sulphur are dissolved in the usual manner, the sulphur separates out and produces a turbidity which interferes with the colour-test for carbon; a fact easily proved by dividing such a solution into two portions, filtering one, and then comparing the colour produced in the filtered and unfiltered solutions. Consequently, if a common steel is compared with a standard of pure steel, the colour intensity is sure to be over-estimated, and *vice versâ*.

D. A. L.

Quantitative Analysis by Electrolysis. By A. CLASSEN and R. SCHELLE (*Ber.*, **21**, 2892—2899).—The current from two of Farbaky and Schenek's accumulators, fully charged by a dynamo giving a current of 20—25 ampères, was employed in making 50 analyses in the course of six days. Four to eight analyses were made simultaneously, and the current was employed continuously day and night, except during the short intervals required for changing the platinum dishes. During this time the strength of the current decreased from 2·05 to 1·92 volt, so that one charge would be sufficient for 60 to 70 analyses. The condition of the accumulator can be ascertained from the specific gravity of the sulphuric acid, which is 1·240 when the accumulator is charged and 1·118 when it is not charged. The precipitated metal is in a more suitable condition than when a battery or dynamo is employed.

Experiments which were made with Neumann's (Abstr., 1888, 529) and Wolff's (*Zeit. ang. Chem.*, 1888, 296) voltameters, employing currents of various strengths, show the necessity of working under the same conditions when repeating electrolytic methods of analysis (compare Classen, *Quantitative Analyse durch Electrolyse*, 2nd ed., 43).

In the separation of antimony from tin in sodium sulphide solution, the solution, freed from antimony, is boiled with ammonium sulphate, and the tin precipitated by electrolysis (compare Abstr., 1884, 932). A simpler and more convenient method is to convert the stannic sulphide into hydrogen stannic oxalate and electrolyse the solution. For this purpose, the solution is acidified with dilute sulphuric acid, and the sulphide oxidised with ammoniacal hydrogen peroxide, or the hot alkaline solution is treated at once with hydrogen peroxide until it becomes colourless, acidified with sulphuric acid, neutralised with ammonia, and more hydrogen peroxide added. The solution is then boiled, filtered, and the residual stannic acid washed off the filter with and dissolved in a hot solution of oxalic acid. If there is a residue of sulphur, it is separated by filtration, washed with a cold saturated solution of hydrogen ammonium oxalate, and the washings added to the filtrate. The solution, which should contain at least 50 c.c. of the hydrogen ammonium oxalate solution, is electrolysed with a current giving 8—10 c.c. of explosive gas per minute.

The electrolytic deposition of copper from its salts, dissolved in a saturated solution of ammonium oxalate, is hastened very considerably if the solution is kept acid, especially towards the end of the operation, by adding excess of a cold, saturated solution of oxalic acid. The smaller the quantity of copper, the more oxalic acid solution may be added. A solution poor in copper can be mixed with the oxalic acid solution at the commencement of the process, but in concentrated solutions, the precipitation must be carried out in a solution as nearly neutral as possible to avoid the separation of copper oxalate. If the copper solution is kept at 40—50°, about two grams of copper are deposited in from 3 to 4 hours. A current giving 3—4 c.c. of explosive gas per minute was employed, and quantitative experiments showed that the whole of the copper is deposited.

F. S. K.

Separation of Calcium, Barium, and Strontium. By KUPFFERSCHLAEGER (*Bull. Soc. Chim.*, **49**, 854—856).—A quantitative analysis of a mixture of the carbonates of barium, strontium, and calcium can be carried out as follows:—The mixture is dissolved in a slight excess of very dilute nitric acid, the solution evaporated to dryness, the residue dissolved in distilled water, and the filtered solution again evaporated to complete dryness. The residue of mixed nitrates is agitated with a small quantity of a mixture of absolute alcohol and ether, and the solvent separated by filtration as soon as the solution becomes clear; this process is repeated three times, the proportion of ether being gradually increased until the mixture contains equal volumes of the constituents. The residual mixture of the nitrates of barium and strontium is dried, dissolved in water, and treated with a cold saturated solution of potassium dichromate. The precipitated barium dichromate is washed with cold, very dilute alcohol, and converted into sulphate by heating with sulphuric acid. The strontium in the filtrate is converted into sulphate by warming the solution with dilute sulphuric acid. A solution of strontium chloride is not precipitated by potassium dichromate. F. S. K.

Volumetric Estimation of Mercuric Chloride. By G. KASSNER (*Arch. Pharm.* [3], **26**, 595—604).—The method promises well for pharmaceutical practice. 50 grams of the organic compound containing mercuric chloride is placed in a porcelain dish without previous division, 500 c.c. of water is added, and the mass is well kneaded with a pestle. 500 c.c. of a solution of 0·4 gram of potassium antimonious tartrate and 1 gram of sodium phosphate, or in place of the latter 1 to 2 grams of sodium acetate, is now added and the kneading continued. A very intimate mixture is thus obtained, and a milky liquid results from the decomposition of the mercuric chloride. About 500 c.c. is now filtered off, and titrated with decinormal iodine solution after the addition of freshly prepared starch solution, and a sufficient quantity of sodium hydrogen carbonate. The iodine employed corresponds to the amount of unchanged tartrate remaining in the filtrate. The reaction is as follows:—$4HgCl_2 + Sb_2O_3 + 2H_2O = 4HCl + Sb_2O_5 + 4HgCl$. The presence of phosphoric and organic acids is admissible, but not of free hydrochloric acid. J. T.

Microchemical Reactions. By A. STRENG (*Jahrb. f. Min.*, 1888, ii, Mem., 142—152; continuation of Abstr., 1886, 487).—For detecting *tin* under the microscope, the author avails himself of the brown colour produced on adding hydrochloric acid and platinum chloride. When the solution is effected, a drop of the liquid is transferred to an object-glass, and a grain of potassium chloride added, and the solution slightly evaporated. In this way, rhombic crystals of potassium stannous chloride ($2KCl + SnCl_2 + H_2O$) are formed. They are mostly combinations of the forms ∞P, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $\bar{P}\infty$, $\breve{P}\infty$. When the stannous chloride has been thus detected, a drop of nitric acid is added, and the solution heated. The stannous chloride is converted into stannic chloride, and the imperfectly soluble salt, K_2SnCl_6 is formed. This crystallises in the regular system, and is perfectly isotropic. This reaction may be employed for detecting stannous and stannic oxides in compounds soluble in hydrochloric acid. Cæsium chloride may be used instead of the isomorphous potassium salt. The author also describes methods for detecting potassium, cæsium, and rubidium, sodium, and silicon. B. H. B.

Detection of small Quantities of Germanium. By K. HAUSHOFER (*Chem. Centr.*, 1888, 867, from *Sitzber. Akad. München*, 1887, 133).

—By heating in an atmosphere of hydrogen sulphide, the germanium in the mineral argyrodite is converted into the sulphide GeS, which is crystalline, and may be detected and recognised by means of the microscope. With concentrated sulphuric acid, it forms a white, non-crystalline substance, with concentrated nitric acid it is converted into the white, crystalline oxide, GeO_2, which is soluble in dilute nitric acid and water, and crystallises out of the solution again on evaporation. Heated in a tube, it sublimes similarly to antimony oxide, but differs from this by its solubility in water, and also by melting to clear colourless drops. It is necessary to apply the potassium iodide test also, as a means of distinguishing it from the mercuric sulphide, which has also been found present in argyrodite. J. W. L.

Characteristic Reaction of Bismuth. By E. Léger (*Bull. Soc. Chim.*, **50**, 91—93).—A solution of bismuth iodide and potassium iodide is sometimes used for detecting alkaloïds, with which it gives orange-yellow precipitates. It is suggested that the reaction should be employed for detecting bismuth. A solution is prepared by dissolving cinchonine (1 gram) and potassium iodide (2 grams) in water (100 c.c.). Other alkaloïds may be used instead of cinchonine, but this seems to give the most sensitive reaction. The reagent must be added in excess; the presence of too much nitric acid, and especially the presence of hydrochloric and sulphuric acids, is to be avoided. Bismuth may be detected in solutions containing only 1 part in 500,000 parts. Solutions which contain other metals besides bismuth are precipitated with hydrogen sulphide, the sulphides of copper, lead, cadmium, mercury, and bismuth converted into nitrates, then into carbonates, and the carbonates of bismuth and lead separated by means of potassium cyanide; these carbonates are converted into chlorides, and the lead chloride separated by means of alcohol. The alcoholic solution is evaporated to dryness, dissolved in a drop of nitric acid and some c.c. of water, and treated with the reagent. Solutions of the salts of mercury, cadmium, silver, copper, and lead also give precipitates of various colours with the cinchonine reagent.
N. H. M.

Determination of Oxygen dissolved in Water. By L. W. Winkler (*Ber.*, **21**, 2846—2854).—The method consists in oxidising an excess of manganese hydroxide in presence of alkali by the oxygen present in a weighed amount of the water; potassium iodide and hydrochloric acid are then added, and the iodine which separates (which is equivalent to the amount of dissolved oxygen) titrated with sodium thiosulphate. A solution of manganous chloride (free from iron) is made of such a strength that 100 c.c. contains 40 grams of the salt ($MnCl_2 + 4H_2O$). The soda must be free from nitrate, and the solution prepared of eight times the normal strength; potassium iodide (10 grams) is dissolved in 100 c.c. of the soda solution, the rest of which is kept. A strong flask of about $\frac{1}{4}$ litre capacity is filled with the water; 1 c.c. of the potassium iodide soda solution is added by means of a pipette reaching nearly to the bottom of the flask, then 1 c.c. of the manganous chloride solution. The flask is closed, care being taken that no bubble of air remains, and the contents mixed.

When the precipitate settles, fuming hydrochloric acid (3 c.c.) is added by means of a pipette similar to those previously used. The flask is again closed, the contents mixed, and the yellow liquid titrated in the usual manner with sodium thiosulphate, the most convenient strength of which is 1/100 normal, so that each c.c. corresponds with 0·055825 c.c. of oxygen (at 0° and 760 mm. pressure).

When the water to be analysed contains much carbonic anhydride, more of the reagent must be added, as manganous carbonate is not oxidised by the oxygen. In the case of waters containing nitrates, the process has to be modified: a soda solution containing no potassium iodide is first added, then hydrochloric acid (twice the amount otherwise used), and after three minutes a solution of potassium iodide. A manganic chloride solution is then prepared as follows:—500 c.c. of distilled water is treated with the pure soda solution (1 c.c.), 5 to 10 drops of the manganous chloride solution, and then sufficient hydrochloric acid is added to dissolve the precipitate. 100 c.c. of this solution is taken out and diluted with distilled water; to the rest, 100 c.c. of the water to be examined is added. After two to three minutes, both solutions are treated with potassium iodide and the iodine which separates determined as usual. From the difference in the amount of thiosulphate used, the correction for 100 c.c. of water is calculated.

Concordant results obtained by the new method are given.

N. H. M.

Ash Determination. By F. A. Flückiger (*Zeit. anal. Chem.*, **27**, 637—638).—The substance is heated in a roomy platinum capsule so gently that carbonisation takes place without combustion. It is then cooled, a copious amount of water is added, and the whole evaporated completely on the water-bath. On reheating the carbonaceous residue very gradually, it burns at a low temperature, and very quickly.

M. J. S.

Wet Methods of Organic Analysis. By J. Messinger (*Ber.*, **21**, 2910—2919).—Organic compounds, as Cross and Bevan have shown (Proc., 1888, 76, and Trans., 1888, 889), are completely oxidised when warmed with chromic acid and concentrated sulphuric acid. If nitrogen is present, it is evolved as such or as ammonia, whilst sulphur, phosphorus, and arsenic are converted into the corresponding acids. Halogens are evolved in the free state, and metals remain as sulphate or, with a large excess of chromic acid, as chromates.

To estimate the quantity of carbon, the substance (0·15—0·35 gram) is weighed in a small bulb or tube, and placed in the apparatus employed by Classen for the estimation of carbonic anhydride (*Quantitative Analyse*, 3rd ed., 239), together with chromic acid (5—6 grams) or powdered potassium dichromate. A gentle stream of air, free from carbonic anhydride, is passed through the apparatus to drive out the carbonic anhydride, the weighed potash bulbs and soda-lime tube are attached, and the latter connected with a calcium chloride tube to prevent absorption of moisture from the air. Concentrated sulphuric acid (30 c.c.) is then poured through the funnel, and the stream of air stopped. The flask is warmed very cautiously until the evolution of carbonic anhydride commences, and then the heating is immediately discontinued until the reaction is almost at an end. The process occupies about two hours. Pure air is passed through the apparatus for half an hour, and the tubes weighed. The results obtained are very satisfactory, except in the case of substances which sublime readily, but great care must be taken when heat is first applied. In analysing volatile substances, the bulb is broken by means of the funnel. If the substance contains halogens, a Dreschler's flask of about 100 c.c. capacity, containing 40 c.c. of concentrated potassium iodide solution, and a small U-tube filled with glass-wool, half of which is moistened with a solution of silver nitrate and half with concentrated sulphuric acid, are interposed between the condenser and the potash bulbs. Quantitative experiments with compounds of the most varied nature gave satisfactory results (compare Cross and Bevan, *loc. cit.*).

Sulphur can be estimated, except in the case of extremely volatile substances, as follows:—The substance (0·15—0·35 gram), together with potassium permanganate (1½—2 grams), and pure potash (0·5 gram) is placed in a flask of 500 c.c. capacity provided with a condenser, water (25—30 c.c.) poured down the condenser, and the mixture heated for 2—3 hours. Concentrated hydrochloric acid is then gradually poured down the condenser into the cold mixture, which should be of a reddish colour, and after the evolution of gas has ceased, the whole is heated until the liquid becomes clear. The sulphuric acid is then precipitated with barium chloride. Potassium dichromate (2—3 grams) and hydrochloric acid (20—25 c.c.: 2 parts concentrated acid, 1 part water) may be employed instead of potassium permanganate and potash. The operation is carried out in the manner described, but after heating for about two hours a few drops of alcohol are added to determine whether all the dichromate has been reduced; if the odour of aldehyde is perceptible, the mixture must be heated again and the test repeated. Both methods can also be employed for the detection of sulphur. Numerous quantitative experiments gave satisfactory results, but in the case of a few sulphones it was found that sulphur cannot be estimated by this method.

Phosphorus, arsenic, and antimony in organic compounds can be estimated by placing the substance (0·3—0·4 gram) with chromic acid (4—5 grams) in a flask provided with a condenser, pouring sulphuric acid (10 c.c., 2 parts concentrated acid, 1 part water) down the condenser, and heating gently. After an hour's time, sulphuric acid (10 c.c.) is added, and the heating continued for about an hour. The mixture must always be heated very carefully, and the cold solution should be perfectly clear. Some antimony compounds require only 1 gram of chromic acid and 10 c.c. of sulphuric acid.

In the estimation of phosphorus, the solution is warmed with ammonium nitrate (3—4 grams) and ammonium molybdate solution (50 c.c.) for 2—3 hours, filtered, the precipitate washed 6 to 8 times by decantation with ammonium nitrate solution (20 grams in 100 c.c. of water), thrown on to a filter, and dissolved in not more than 40—50 c.c. of warm dilute (2 per cent.) ammonia; a concentrated solution of citric acid (4—5 drops) is added to the filtrate, and the phosphoric acid precipitated with magnesia mixture.

In estimating arsenic, the solution is diluted to about 100 c.c., heated to about 70°, and the arsenic precipitated with hydrogen sulphide. The precipitate is washed with water containing hydrogen sulphide until free from chromium salts, and then converted into arsenic acid by means of ammoniacal hydrogen peroxide (compare Classen, Abstr., 1883, 934). After boiling for an hour, ammonia is added to the filtered solution, and the arsenic precipitated with magnesia mixture. Antimony is estimated by adding potash and excess of sodium sulphide, boiling for half an hour, and precipitating the metal electrolytically.

Metals are estimated by mixing the solution with excess of ammonium oxalate and precipitating electrolytically. Halogens can be detected by warming the substance (1—2 mgrms.) with chromic acid and sulphuric acid, and passing the gas evolved into a dilute solution of potassium iodide; quantitative experiments gave unsatisfactory results. F. S. K.

The Safety of Commercial Kerosene Oils. By S. B. Newbury and W. P. Cutter (*Amer. Chem. J.*, 356—362).—Although oils are regularly tested for their flashing points and conclusions drawn as to their being safe for burning in lamps, it is noteworthy that many modern lamps heat their reservoir of oil to temperatures above the legal flashing point, and that there are not sufficient experimental data to allow of the correct interpretation of the flashing point determinations into terms expressing the inability of such oils to form explosive mixtures of vapour with air. All hydrocarbons up to and including octane, form at ordinary temperatures mixtures that can be exploded; nonane mixtures (b. p. 148—150°) explode sharply at 79° F., and decane at 104° F.

The addition of small quantities of low-boiling oils materially lowers the flashing point of another sample. Thus a sample flashing at 212° F. was made to flash at 145° F. by the addition of 5 per cent. of heptane; at 110° F. by the addition of 5 per cent. pentane or hexane, or 10 per cent. heptane; at 96° F. by the addition of 15 per cent. heptane; and at ordinary temperatures by the addition of 10 per cent. pentane or hexane, or 20 per cent. heptane. The temperatures at which an oil may be kindled in an open vessel approaches the more nearly to the flashing point the more homogeneous the oil is. The flashing point of an ordinary oil may be materially raised, with but little diminution of weight, by passing a current of air through it for several hours. H. B.

Solubility and Estimation of Paraffin. By B. Pawlewski and J. Filemonowicz (*Ber.*, **21**, 2973—2976).—The following table gives the solubility at 20° of ozokerit paraffin of sp. gr. 0·9170 at 20°, melting at 64—65°, and solidifying at 61—63°:—

Solvent.	Paraffin (grams), dissolved by		Weight of solvent required to dissolve completely 1 part of paraffin.
	100 grams.	100 c.c.	
Carbon bisulphide	12·99	—	7·6
Light petroleum, up to 75° C., sp. gr. 0·7233	11·73	8·48	8·5
Turpentine oil, sp. gr. 0·857; b. p. 158—166°	6·06	5·21	16·1
Cumene (comm.), up to 160°, sp. gr. = 0·867	4·28	3·72	23·4
Cumene (frac.), 150—160°, sp. gr. = 0·847	3·99	3·39	25·0
Xylene (comm.), 135—143°, sp. gr. = 0·866	3·95	3·43	25·1
„ (frac.), 136—138°, sp. gr. = 0·864	4·39	3·77	22·7
Toluene (comm.), 108—110°, sp. gr. = 0·866	3·83	3·34	26·1
„ (frac.), 108·5—109·5°, sp. gr. = 0·866	3·92	3·41	25·5
Chloroform	2·42	3·61	41·3
Benzene	1·99	1·75	50·3
Ethyl ether	1·95	—	50·8
Isobutyl alcohol (comm.), sp. gr. = 0·804	0·285	0·228	352·9
Acetone, 55·5—56·5°, sp. gr. = 0·797	0·262	0·209	378·7
Ethyl acetate	0·238	—	419·0
Ethyl alcohol, 99·5° Tr.	0·219	—	453·6
Amyl alcohol, 127—129°, sp. gr. = 0·813	0·202	0·164	495·3
Propionic acid	0·165	—	595·3
Propyl alcohol	0·141	—	709·4
Methyl alcohol, 65·5 - 66·5°, sp. gr. = 0·798	0·071	0·056	1447·5
Methyl formate	0·060	—	1648·7
Glacial acetic acid	0·060	0·063	1668·6
Ethyl alcohol, 94·5° Tr.	0·046	—	2149·5
Acetic anhydride	0·025	—	3856·2
Formic acid (cryst.)	0·013	0·015	7689·2
Ethyl alcohol, 75° Tr.	0·0003	—	330000·0

The liquid constituents present in many products of the petroleum or ozokerit industry are soluble in glacial acetic acid, whereas vaselin, cerisin, ozokerit, and paraffin are almost insoluble. To estimate the quantity of solid paraffin in petroleum, lubricating oils, mineral oils, vaselin, &c., 5—20 c.c. of the mixture is well shaken with 100—200 c.c. of glacial acetic acid, the residual paraffin thrown on to a weighed filter, washed two or three times with glacial acetic acid, and then two or three times with alcohol of 75° Tr., dried and weighed, or the residual paraffin is washed, dissolved in benzene or ether, the solution evaporated, and the residue weighed. This method is quick and accurate, and can be carried out at the ordinary temperature. F. S. K.

Analysis of a Mixture of Silver Chloride, Cyanide, Thiocyanate, Ferricyanide, and Ferrocyanide. By J. Teissier (*Bull. Soc. Chim.*, **50**, 104—106).—The mixture occurs in the analysis of materials used in the purification of coal-gas. Sodium carbonate is heated in a crucible until anhydrous, the weighed substance and some potassium nitrate are added, and the whole is heated. The product is extracted with water, which leaves a residue of pure silver and ferric oxide. In the solution, sulphur is determined as barium sulphate and chlorine as silver chloride. The residue is dissolved in nitric acid, the silver determined as chloride, and the iron as sesquioxide. Equations are given by means of which the amount of each salt present in the mixture is calculated. N. H. M.

Estimation of Paranitrotoluene. By F. Reverdin and C. de la Harpe (*Bull. Soc. Chim.*, **50**, 44—46).—The method is based on the fact that paranitrotoluenesulphonic acid is readily converted by boiling with soda into dinitrosulphostilbene which yields a red colour when dissolved in alkali, whilst orthonitrotoluenesulphonic acid is not attacked by soda, and the alkaline solution is yellow. 2 c.c. of pure orthonitrotoluene is heated in a water-bath with 6 c.c. of sulphuric acid (containing 25 per cent. of anhydride) for three hours, the product cooled and diluted to 1 litre. In a similar manner a mixture of orthonitrotoluene (96 parts) and paranitrotoluene (4 parts) is sulphonated and the product diluted to 200 c.c. In determining the amount of paranitrotoluene, the substance and nitrotoluene (containing 4 per cent. of the para-compound) are sulphonated, the products diluted to 200 c.c., and the colours compared which are obtained by mixing 1 c.c. of each solution with 5 c.c. of aqueous soda. If the sample to be analysed gives a stronger colour, a measured quantity (20 to 50 c.c.) is progressively diluted with the solution of orthonitrotoluenesulphonic acid until 1 c.c. when heated with 5 c.c. of aqueous soda gives the same amount of colour as the solution containing 4 per cent. The percentage of paranitrotoluene can then be calculated. N. H. M.

Detection of Methyl Alcohol in Wood Spirit. By J. Habermann (*Zeit. anal. Chem.*, **27**, 663, from *Verhandl. nat. Ver. Brünn*, **26**).—Commercial methyl alcohol contains impurities which reduce permanganate energetically. Cazeneuve and Cotton shake 10 c.c. of the spirit to be tested with 1 c.c. of a 0·1 per cent. solution of permanganate at 20°. If wood spirit is present, decolorisation takes place immediately; with pure alcohol, 20 minutes is required. Ethereal oils, which may be present in spirit or brandy, and would cause a similar reduction, may be removed by shaking the spirit twice with half its volume of the purest olive oil and then filtering through a well wetted filter. If sugar is present, the spirit must be distilled.

M. J. S.

Composition of Natural Brandies and the Way of Distinguishing them. By X. Rocques (*Bull. Soc. Chim.*, **50**, 157—164).—500 c.c. of the brandy is distilled in a Le Bel-Henniger apparatus and nine fractions of 50 c.c. each collected, the temperatures being noted. Each fraction is subjected to the following tests:—(1) Rosaniline bisulphite, (2) aniline acetate, (3) sulphuric acid, (4) permanganate, (5) ammoniacal silver nitrate solution. The results of several analyses of brandies are given in tables.

N. H. M.

Estimation of Sugar in Presence of Carbohydrates. By R. W. BISHOP (*Chem. Centr.*, 1888, 952—953, from *Msc. Mon. Sci.*, **32**, 558).—The author has carried out a number of experiments with a view to determine the conditions under which inversion may be completed without at the same time damaging the accompanying carbohydrates. It was found that sulphuric acid has a greater power of inversion than hydrochloric acid, but it appears that hydrochloric acid is the best for the conversion of starch into dextrose. Prolonged heating of inverted sugar with the acid seems to act on the lævulose rather strongly, and the solution becomes less lævorotatory and eventually dextrorotatory. For the inversion of cane-sugar, 0·5 c.c. of hydrochloric acid is sufficient, and the heating is continued for 10 minutes at 95°. For the conversion of dextrin, the solution should not contain more than 1—3 grams of carbohydrates in 50 c.c. The inversion is performed by adding 2 c.c. of hydrochloric acid and heating for three hours at 95°. J. W. L.

Detection of Sugar in Urine. By C. SCHWARZ (*Arch. Pharm.* [3], **26**, 796, from *Pharm. Zeit.*, **33**, 465).—1 to 2 c.c. of lead acetate is added to 10 c.c. of urine and filtered; 5 c.c. of the filtrate is mixed with 5 c.c. of normal potash solution and one or two drops of phenylhydrazine, well shaken and vigorously boiled; in the presence of sugar, the liquid becomes lemon- to orange-yellow, and becomes opaque on adding an excess of acetic acid owing to the immediate formation of a finely divided yellow precipitate. In the absence of sugar, this precipitate never occurs with urine. J. T.

Detection of Chloral or Chloroform in Liquids. By C. SCHWARZ (*Zeit. anal. Chem.*, **27**, 668—669, from *Pharm. Zeit.*, **33**, 419).—Either of these substances when boiled with resorcinol and an excess of soda gives a red colour, which disappears on acidifying and is restored by alkalis. If, on the other hand, an excess of resorcinol and only a drop or two of soda solution is used, the product is a yellowish-red solution with intense yellowish-green fluorescence. 0·0001 gram of chloral hydrate in 1 c.c. gives this reaction very distinctly when vigorously boiled with 0·05 gram of resorcinol and five drops of soda solution. M. J. S.

Modification of the Reichert-Meissl Method of Butter Analysis. By M. MANSFELD (*Chem. Centr.*, 1888, 870—871, from *Milch Zeit.*, **17**, 281—283).—In order to obviate the possible error arising from the use of alcohol in the saponification of the butter-fat, the author has tried the use of alkali alone, the latter being added to the fat in a small flask and heated on the water-bath for two hours, at the end of which time the saponification is complete, and the process is finished as Wollny prescribes. J. W. L.

Densities and Refractive Indices of Certain Oils. By J. H. LONG (*Amer. Chem. J.*, **10**, 392—405).—The following values are obtained—the densities at 20° being compared with water at 4° as unity, and the substance weighed in a vacuum; the refractive indices are for sodium light at 20° :—

Olive oil	0·9130	Ref. index	1·4703
Cotton-seed oil	0·9191		1·4732
Sesame oil	0·9191		1·4740
Mustard oil........	0·9121		1·4742
Castor oil..........	0·9589		1·4791
Lard oil	0·9122		1·4686
Peanut oil	0·9173		1·4717

The densities and refractive indices are also given for other temperatures than 20°. In nearly all cases, the variations due to temperature are the same, namely, about —0·00068 in density and —0·0004 in refraction for each rise of 1°. The author believes such determinations may prove of value in the identification of other oils. H. B.

Bechi's Newest Method for the Detection of Cotton-seed Oil in Mixtures. By G. BIZIO (*Chem. Centr.*, 1888, 873, from *Atti Inst. Veneto* [6], 6).—The author finds that pure olive oil gives Bechi's new cotton-seed oil reaction with slightly acid silver nitrate, whilst, on the other hand, he finds that there are some cotton-seed oils which do not give the reaction at all. J. W. L.

Qualitative Test for Resin Oil in Vegetable and Mineral Oils. By HOLDE (*Chem. Centr.*, 1888, 952, from *Pharm. Zeit.*, **33**, 298).—Whereas Storch's reagent (concentrated sulphuric acid and anhydrous acetic acid) for the detection of resin oil is not always admissible, the author recommends sulphuric acid of sp. gr. 1·53, which produces a violet coloration with resin oil. If the oil under examination becomes so dark-coloured with sulphuric acid as to interfere with the reaction, the resin oil may first be extracted with alcohol, when the colour test is readily performed. J. W. L.

Test for "Saccharin." By D. LINDO (*Chem. News*, **58**, 155).—The author modifies his test for "saccharin" (Abstr., 1888, 1350). After evaporating to dryness with nitric acid on a water-bath, a few drops of alcoholic potash is added to the cold residue; when this is heated, a greater variety of colours is obtained than by following the original directions. D. A. L.

Recent Processes for Testing Quinine. By W. LENZ (*Zeit. anal. Chem.*, **27**, 549—631).—The foreign alkaloïds in commercial quinine consist chiefly of cinchonidine and hydro-bases. Four principal methods are in use for the determination of these. In all these methods, a product ("Nebenalkaloïde") is obtained, containing the greater part of the impurities together with a certain quantity of quinine. In this product, the cinchonidine is determined by the "tetrasulphate process." 1 gram of the mixture is dissolved in 9 grams of absolute alcohol and 3 grams of 50 per cent. sulphuric acid. The mixture is kept at 0° for 24 hours, the acid liquid is removed by suction, the crystals are washed with a little absolute alcohol, and then air-dried. They are then dissolved in water, and the base is precipitated by excess of sodium carbonate. It is dried first over sulphuric acid, and then at 115°. A correction (the amount of which depends on the percentage of cinchonidine found) must be applied. The author gives a curve for the purpose. The cinchonidine is very nearly pure. The hydro-bases are determined approximately by oxidising the quinine and cinchonidine in acid solution by a 1 per cent. solution of potassium permanganate, rendering alkaline, and shaking with ether, followed by chloroform. The residues from these solutions, although very impure, are regarded as hydroquinine.

For the "chromate process" of De Vrij see Abstr., 1887, 404; for the "oxalate test," see Schaefer (Abstr., 1887, 623). The amount of oxalate prescribed is insufficient for samples containing less than 15 per cent. of water, and the cooling at 20° should be prolonged to one hour. Schaefer's correction of 0·04 gram per 100 c.c. appears to be too large.

In Hesse's "bisulphate process" 5 grams of quinine sulphate is dissolved in 12 c.c. of normal sulphuric acid by warming, and the solution is allowed to crystallise in a narrow-necked funnel in a cold place. The mother-liquor is withdrawn by a filter-pump into a graduated cylinder, and the crystals washed with 3 c.c. of water. This solution is shaken with 16 c.c. of ether (0·721—0·728), then 3 c.c. of ammonia (0·96) added, again shaken, and left for 24 hours. The ether is removed by a pipette, the crystals are collected on a filter, washed with water saturated with ether, dried between filter-paper, washed again with ether, and dried.

In the "crystallisation process" of Paul and Hesse, 5 grams of quinine sulphate is dissolved in boiling water, and crystallised out four times, using in the first case 150 c.c., next 130 c.c., and then twice 120 c.c. The united mother-liquors are evaporated at a low temperature almost to dryness, the residue dissolved in the smallest possible quantity of dilute sulphuric acid, made up to 20 c.c., and shaken with ether and excess of ammonia. The crystals which form are treated as in the bisulphate test. The hydro-bases crystallise in part with the quinine, therefore the mother-liquor should not be used for their determination.

The chromate process gives very varying results, but on the average gives the highest yield of cinchonidine, especially with the purer samples. The oxalate test gives the lowest numbers, but they are more concordant than those of the chromate process. The composition of the bye-product is, however, variable. The bisulphate test gives results varying considerably. The alkaloïds in the ethereal solution ought to be submitted to the process a second and even a third time, but even with this improvement the whole of the cinchonidine is not obtained, and the results vary much, but the composition of the bye-product is more uniform than in the other processes. The crystallisation test has the same advantages as the bisulphate test if the crystallisation is repeated often enough, and is the process which is least influenced by the presence of hydro-bases. It is, however, tedious. The process of the German Pharmacopœia depends on the fact that the precipitate produced by ammonia in solutions of the alkaloïds is soluble in excess of ammonia, but that much more ammonia is required for quinine than for the other alkaloïds. The excess of ammonia required varies, however, very considerably with the temperature. M. J. S.

Method for Recognising the Adulteration of Pepper by the Addition of Ground Olive Stones. By GILLET (*Bull. Soc. Chim.*, **50**, 173—174).—When 1 gram of olive stones is treated with 1 c.c. of a 5 per cent. iodine tincture, it acquires, after a quarter of an hour, a yellowish colour, whilst pepper is coloured brown or maroon. A series of mixtures of pepper with 5, 10, 15, and 20 per cent. of olive stones are prepared and coloured with iodine tincture. It is then easy to determine the amount of olive stones in samples of pepper by comparing the colour obtained with these types. N. H. M.

A New Test for the Blood in Carbonic Oxide Poisoning. By K. KATAYAMA (*Virchow's Archiv*, **114**, 53—64).—When ammonium sulphide holding sulphur in solution and acetic acid are added to blood containing carbonic oxide, the result is a beautiful clear red or rose colour; whereas normal blood becomes greenish-grey, or reddish-green-grey on the addition of the same reagents. On examining these liquids spectroscopically, it is found that both in the case of normal and carbonic oxide blood the absorption-spectrum indicates that a mixture of two substances is present. In the case of normal blood, there is a band between C and D and another between D and E; this last becomes double on shaking up the mixture with air. In other words, there is a mixture of sulphur methæmoglobin (see Hoppe-Seyler, *Physiol. Chem.*, 386) and reduced hæmoglobin.

In the case of carbonic oxide there are three bands: one between C and D, due to sulphur methæmoglobin, and two between D and E, due to carbonic oxide hæmoglobin. That is to say, in spite of the presence of sulphur methæmoglobin, the liquid does not become greenish, but remains red, the colour of carbonic oxide hæmoglobin overpowering the olive-green of the sulphur methæmoglobin. This test is stated to be more delicate than Hoppe-Seyler's (Abstr., 1888, 540), and is obtained with a mixture which contains one part of carbonic oxide blood to five parts of normal blood. W. D. H.

Estimation of Albumin in Urine. By H. SCHAUMANN (*Zeit. anal. Chem.*, **27**, 635—636).—The estimation of albumin is much accelerated by collecting it, not on a paper filter, but in a filter-tube plugged with cotton-wool and connected with a filter-pump. When the washing with hot water is complete, a calcium chloride tube is connected, and dry air is drawn over the albumin whilst gradually raising its temperature to 110°. M. J. S.

General and Physical Chemistry.

Spectrum of Magnesium. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **44**, 241—252).—When an electric arc is formed between magnesium electrodes, most of the lines produced by the spark discharge are observed. The larger number of lines with an arc discharge may be due not to lowness of temperature, but to the greater mass of incandescent matter, and to a wider range of temperature at different portions of the discharge, recombinations occurring at its edge. The electric discharge itself may also give rise to vibrations distinct from those due to heat. The seven bands in the green are due to the oxide, as they are only produced in the presence of oxygen or its compounds. If a piece of burnt magnesium wire be heated in the oxyhydrogen flame, the spectrum of magnesium is produced, the metallic lines appearing if the hydrogen is in excess. The triplet near M which is produced when magnesium is burnt, is found to be produced in the arc between magnesium electrodes and in many other cases when oxygen is present, but not in an atmosphere of nitrogen or hydrogen, hence it is due to the oxide. Vacuous tubes are found to be very untrustworthy for the ultra-violet spectra, as the water-spectrum and lines of nitrogen are nearly always present, and the spectra sometimes vary unaccountably. A pump is described in which rubber connections and free contact of the mercury with air are avoided. H. K. T.

Ultra-violet Spectra of Nickel and Cobalt. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **43**, 430).—A comparison is made between a plane Rowland's grating with a goniometer and the concave grating (20 feet focal length) used by Bell. The results agree very closely, the concave grating gives more light, and is more suitable for complicated spectra, as the overlapping spectra of different orders are not all in focus at once.

Ultra-violet lines of cobalt and nickel are compared. The coincidences are not greater than the theory of chances would allow, and do not correspond with their chemical relationship. H. K. T.

Two-fluid Cells. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, **43**, 489—493).—Cells are set up consisting of platinum plates in acid and alkaline solutions, with the further addition either of oxidising agents to the acid solution or of reducing agents to the alkaline solution. Currents are produced, in the first case with evolution of oxygen from the alkaline solution, in the second with evolution of hydrogen from the acid solution. The quantity of gas evolved was equivalent to the current. The acid and alkali were sulphuric acid and potassium hydroxide respectively; the oxidising agents being potassium permanganate, dichromate, and ferricyanide, ferric chloride, and solutions of chlorine and bromine and the reducing agents sodium hyposulphite, pyrogallol, cuprous chloride, and ferrous sulphate and ammonium chloride in ammoniacal solution. Hydrogen was not evolved with sodium sulphite or hypophosphite, potassium ferrocyanide, or manganous hydroxide in ammoniacal ammonium chloride, nor was oxygen with barium dioxide and sulphuric acid, or with hydrochloric acid and iodine. On the other hand, an aëration plate of platinum sponge gave a current four times as great. Plates of oxidisable metals in alkaline solution could be substituted for the reducing substance, hydrogen being evolved in the acid solution; this was particularly the case when potassium cyanide was used. Gold, silver, and palladium in cyanide solution gave hydrogen, but platinum and iron were ineffective. When both oxidising and reducing agents are used, comparatively powerful currents are produced.

H. K. T.

Effect of Chlorine on the Electromotive Force of a Voltaic Couple. By G. GORE (*Proc. Roy. Soc.*, **44**, 151—152).—If the electromotive force of a small magnesium-platinum couple in distilled water is balanced through a galvanometer and dilute chlorine-water is gradually added, the electromotive force does not alter at first, but after a certain point has been reached (1 in 17,000 millions) it begins to increase rapidly. In this way, the one ten-thousand-millionth of a grain of chlorine in 0·1 c.c. of water can be detected. Other electrolytes give the same reaction, but require a larger quantity of dissolved substance.

H. K. T.

Development of Voltaic Electricity by Atmospheric Oxidation. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, **44**, 182—200).—The electromotive force of cells in which aëration plates are used, falls off very rapidly if the current density exceeds a certain amount. When oxidisable liquids are used, it is difficult to determine, as it appears to vary with the nature of the aëration plate, and also with the incorrodible plate in the liquid to be oxidised. For determining these electromotive forces, an arrangement is used in which the aëration plate can be kept undisturbed, and in which the oxidisable substances are protected from alterations of temperature, impurities from the air, &c. After a few hours or days, the currents become constant. In these cells, variation of the aëration plate produces a difference in the electromotive force independent of the oxidisable plate used; similarly the effect of varying the metal is independent of the aëration plate. The nature and strength of the liquid affects the results to some extent. Tables of results are given. The electromotive force actually generated falls very considerably short of that corresponding with the chemical change, especially when the current density is large. With silver as the oxidisable plate, however, the electromotive force is higher than the theoretical, this being due to the high negative value of the thermovoltaic constant of silver in contact with sulphuric acid. When oxygen was substituted for air over the aëration plate, a slight rise in the electromotive force was observed. With aëration plates immersed in coal-gas or hydrogen, and opposed to a platinum plate in alkaline permanganate or in sulphuric acid and potassium dichromate, very weak and variable currents were observed. The same was the case with cells formed of aëration plates in hydrogen and air respectively. H. K. T.

Electrolytic Conductivity of Rock Crystal. By E. WARBURG and F. TEGETMEIER (*Ann. Phys. Chem.* [2], **35**, 455—467).—In a former paper (*ibid.* [2], **32**, 447), the authors showed that a slice of rock crystal cut perpendicularly to the principal axis, and having its ends covered with layers of gold or plumbago, when subjected at a temperature of about 230° to a long-continued E.M.F. of considerable intensity, had its conductivity permanently reduced to a small fraction of its original amount. In directions perpendicular to the axis, rock crystal, even at higher temperatures, has little or no conductivity.

As the result of their further investigations, the authors have arrived at the conclusions that—

(1.) The electrolytic conductivity of rock crystal in the direction of the principal axis is, at high temperatures, about the same as that of ordinary glass.

(2.) When a slice cut perpendicularly to the axis is electrolysed, sodium-amalgam being used as the anode, sodium migrates through the slice, its amount being in accordance with Faraday's law, and the weight of the slice remains unchanged.

(3.) Even at high temperatures, rock crystal acts as a good insulator with respect to an E.M.F. in a direction perpendicular to the principal axis.

When sodium-amalgam was used as the anode in an experiment lasting for three days, at a temperature of 250°, 88 milligrams of silver were deposited in a silver voltameter in the circuit, and the only substance which could be detected at the cathode was sodium.

When potassium was used in the place of sodium, it was found that after 40 hours the current had sunk to about the hundredth part of its original value, only 2 milligrams of silver were separated, and no potassium could be detected at the cathode, even by means of the spectroscope. The authors therefore conclude that the conductivity is due to the presence of sodium, in the form of Na_2SiO_3, which was shown, by an analysis specially made by Baumann, to be present in the crystal employed in the proportion of 1 part in 2300, so that the crystal might be regarded as a very dilute solution of this salt.

The electrolytic character of the conductivity was further confirmed by the fact that a cell giving an E.M.F. of from 1·3 to 2 volts could be formed of mercury, a slice of quartz at a temperature of 225°, cut perpendicularly to the axis, and sodium-amalgam.

According to Clausius's theory of electrolysis, the fact of electrolytic conduction only taking place in the direction of the principal axis would tend to the inference that in the case of rock crystal not traversed by an electric current, the interchange of atoms between the molecules can only take place, at any rate to a sensible extent, in the direction of the principal axis.

A confirmation of this inference is found in the fact first noted by Salm-Horstmar (*Ann. Phys. Chem.*, **120**, 334), that the action of hydrofluoric acid on rock crystal is much greater in the direction of the axis than perpendicular to this axis. The authors have themselves made experiments to test the truth of this statement, and the results are in agreement with those of Salm-Horstmar.

It would appear from the results obtained in the paper, that the silicate Na_2SiO_3 contained in the crystal must partake of its crystalline structure. G. W. T.

Effect of Occluded Gases on the Thermoelectric Properties of Compounds. By J. MONCKMAN (*Proc. Roy. Soc.*, **44**, 220—236). —When a portion of platinum or palladium wire is charged with hydrogen by electrolysis, and the wire afterwards heated, a current passes from the protected to the unprotected part. The same occurs with rods of carbon after charging and pressing together, the current passing from the hydrogen to the oxygen. The wires and rods are found to have an increased resistance, that of the oxygen rod being the greatest. The effect disappears after short circuiting. If the wires or rods be charged twice in opposite directions, the effect disappears, unless the second charging is of very short duration; in this case, a reversal takes place. With carbon rods at different temperatures in contact, reversal occurs at 250°; with a thermoelectric couple of carbon and platinum, the thermoelectric line rises below 250°, and falls above that temperature. The rate of decrease of resistance of carbon diminishes as the temperature rises to 250°, but increases afterwards. The rate of expansion increases as the temperature rises to 250°, but afterwards decreases. The specific heat increases fairly regularly up to 250°, but above that temperature falls to half. Experiments were also made with graphite rods. H. K. T.

Electrochemical Effects on Magnetising Iron. By T. ANDREWS (*Proc. Roy. Soc.*, **44**, 152—168).—A magnetised and an unmagnetised bar of iron or steel are immersed in different reagents, and the current produced noted. The amount varies considerably, but is large in the case of bromine, salts of copper, and nitric acid. The result is dependent both on the strength of the solution and the degree of magnetisation. With powerful oxidisers, the magnetised bar is generally electropositive, but becomes electronegative with sulphuric acid, dilute hydrochloric acid, and ferric chloride and chlorine. In the last-named instances, the effect may be due to the diamagnetic properties of the solutions, or of the gases evolved. With ferric chloride alone, the magnetised bar is electropositive, with chlorine electronegative, with the two together, electronegative until the chlorine is exhausted, when it becomes electropositive. In the same bar, local currents are produced from the more magnetised portions to the less. These may cause the magnetised bar to be acted on to a greater extent than the unmagnetised. In strong nitric acid, a current is produced from the magnetised to the unmagnetised bar. H. K. T.

Specific Heat of some Solid Organic Compounds. By H. HESS (*Ann. Phys. Chem.* [2], **35**, 410—429).—The author states that, with the exception of some investigations by De Heen (*Bull acad. roy. belg.*, **5**) and A. Battelli (*Atti R. Inst. Veneto* [6], **3**), he has not been able to find any account of investigations of the specific heats of solid organic compounds, and he therefore undertook the present investigation with a view especially of determining the manner in which the specific heats of solid organic substances depend on temperature.

The author gives a number of curves showing the relation between specific heat and temperature in the substances examined, temperatures being taken as ordinates, and the corresponding specific heats as abscissæ. The curves he finds to be sensibly straight lines intersecting the specific heat axis above the zero point, so that the specific heat

Name of substance.	Mean specific heat.		Temperature coefficient.		
	Temperature limits.	*c*.	Temperature limits.	*b*.	Means.
Oxalic acid....	0° to 50°	0·3359	50° to 75°	0·000864	*b* = 0·000835
	0 ,, 75	0·3575	75 ,, 94	0·000801	
	0 ,, 94	0·3728	50 ,, 94	0·000839	
Malonic acid ..	0 ,, 50	0·2832	50 ,, 94	0·000680	*b* = 0·000719
	0 ,, 94	0·3131	94 ,, 110	0·000771	
	0 ,, 110	0·3262	50 ,, 110	0·000705	
Succinic acid ..	0 ,, 50	0·2898	50 ,, 94	0·000805	*b* = 0·000759
	0 ,, 94	0·3252	94 ,, 150	0·000711	
	0 ,, 150	0·3650	50 ,, 150	0·000762	
Isosuccinic acid	0 ,, 50	0·3372	50 ,, 75	0·000512	*b* = 0·000609
	0 ,, 75	0·3500	75 ,, 94	0·000716	
	0 ,, 94	0·3636	50 ,, 94	0·000600	
Glutaric acid (solid)	0 ,, 50	0·3081	50 ,, 75	0·000504	*b* = 0·000901
	0 ,, 75	0·3207	75 ,, 94	0·001337	
	0 ,, 94	0·3461	50 ,, 94	0·000864	
Glutaric acid (liquid)	0 ,, 99·3	0·7285	99 ,, 130	0·000710	*b* = 0·000710
	0 ,, 130	0·7503			
Pyrotartaric acid	0 ,, 50	0·3098	50 ,, 75	0·000676	*b* = 0·000842
	0 ,, 75	0·3267	75 ,, 105	0·001027	
	0 ,, 94	0·3448	50 ,, 94	0·000796	
	0 ,, 105	0·3575	50 ,, 105	0·000867	
Dimethylmalonic acid	0 ,, 50	0·3096	50 ,, 94	0·000859	*b* = 0·000859
	0 ,, 94	0·3474			
Sugar	0 ,, 75	0·3037	75 ,, 94	0·000842	*b* = 0·000841
	0 ,, 94	0·3197	75 ,, 113	0·000789	
	0 ,, 113	0·3337	94 ,, 130	0·000872	
	0 ,, 130	0·3511	75 ,, 130	0·000862	
Benzoic acid (solid)	0 ,, 50	0·2571	50 ,, 94	0·00124	*b* = 0·00125
	0 ,, 94	0·3118	94 ,, 110	0·00126	
	0 ,, 130	0·3319	50 ,, 110	0·00125	
Benzoic acid (liquid)	0 ,, 122	0·5072	122 ,, 136	0·00131	*b* = 0·00131
	0 ,, 136	0·5256			
Phthalic acid ..	0 ,, 75	0·2559	75 ,, 119	0·000689	*b* = 0·000724
	0 ,, 119	0·2862	119 ,, 150	0·000764	
	0 ,, 150	0·3099	75 ,, 150	0·000720	

can be represented by a formula of the form $a + bt$. The results obtained are given in tabular form (p. 93), c representing the mean specific heat between the temperature limits indicated, and b the temperature coefficient.

The values obtained by assuming the true specific heat to be represented by a formula of the form $a + bt$ are given in the second table, under the head of "observed specific heat," the column headed "calculated specific heat" being calculated from Kopp's law, that the molecular heat of a body is equal to the sum of the atomic heats of its constituents. The atomic heats of carbon, hydrogen, and oxygen respectively are taken as 1·8, 2·3, and 4·0. The column headed t gives the temperature at which the observed and calculated specific heats are equal, and it will be seen that with the exception of oxalic and isosuccinic acids, the different substances obey Kopp's law for some temperature within the limits 35° and 50°.

Kopp's law might be generalised if we could assume the specific heats of carbon, hydrogen, and oxygen to be functions of the temperature, but this would not lead to correct general formulæ, for Regnault (*Compt. rend.*, **26**, 311) and E. Wiedemann (*Ann. Phys. Chem.* **157**, 1) have shown that the specific heats of hydrogen and oxygen are sensibly independent of the temperature, and although H. F. Weber has shown (*Ann. Phys. Chem.*, **147**, 362) that the specific heat of carbon increases considerably with the temperature, this increase would not be sufficient to account for the observed increase in the temperature coefficient.

Name of substance.	Specific heat.		t.
	Calculated.	Observed.	
Oxalic acid	0·2689	0·2941 + 0·00167t	−15·1°
Malonic acid	0·2942	0·2473 + 0·00144t	+32·6
Succinic acid	0·3136	0·2518 + 0·00152t	+40·7
Isosuccinic acid	„	0·3067 + 0·00122t	+ 5·7
Glutaric acid (solid)	0·3288	0·2620 + 0·00180t	+37·1
Pyrotartaric acid	„	0·2677 + 0·00168t	+36·4
Dimethylmalonic acid	„	0·2666 + 0·00172t	+36·2
Sugar	0·3240	0·2387 + 0·00173t	+49·3
Benzoic acid	0·2820	0·1946 + 0·00250t	+35·0
Phthalic acid	0·2602	0·2016 + 0·00145t	+40·4
Glutaric acid (liquid)	—	0·6580 + 0·00142t	—
Benzoic acid	—	0·3474 + 0·00262t	—

The author's results show that there are often considerable differences in the specific heats of different isomeric compounds.

G. W. T.

Evolution of Gases from Homogeneous Liquids. By V. H. Veley (*Proc. Roy. Soc.*, **44**, 239—240).—The addition of finely divided substances is found to increase the rate of evolution of gases from liquids in which they are formed. When the temperature remains the same, the rate of evolution rises slowly until a maximum is reached, which is maintained for some time. The rate then decreases proportionally to the diminution in mass. The phenomenon repeats itself when the temperature is lowered and then raised to its former point, and also when the pressure is suddenly increased. The reduction of the pressure to a fraction of an atmosphere produces no permanent effect. The rate of decomposition of formic acid into carbonic anhydride and water is also examined, and is found to agree with the equation $\log(\tau + t) + \log r = \log c$, where τ is the time from the commencement of the observations, t the interval of time from the moment of commencement up to the moment at which the time required for unit change is *nil*, r the mass at the end of each observation, and c a constant. The curve of rate of change conforms with the law $dr/d\tau = -r^2/c$, which expresses the rate at which equivalent masses react on one another. Hence it is presumable that equivalent masses react, and that the change is represented by the equations $HCO{\cdot}OH + HCO{\cdot}OH = HCO{\cdot}O{\cdot}CHO + H_2O$ and $HCO{\cdot}O{\cdot}CHO = 2CO + H_2O$, a reaction similar to the production of ethyl formate from formic acid and alcohol. H. K. T.

Properties of Matter in the Gaseous and Liquid State under Various Conditions of Temperature and Pressure. By the late T. ANDREWS (*Ann. Chim. Phys.* [6], **13**, 411—432).—Regnault (*Mem. Acad. Sci.*, **26**, 680—696) made a series of experiments to determine the tension of a mixture of a gas and a vapour, such as nitrogen or air, and the vapour of water or some more volatile liquid, and came to the conclusion that Dalton's law of partial pressures may be considered theoretically correct in the case of such mixtures, and that probably this law could be proved to be correct experimentally if the mixture of gas and vapour could be enclosed in a vessel the interior surface of which was composed of the volatile liquid. He also found that, under pressures varying from $\frac{2}{3}$ to 2 atmospheres, the compressibility of a mixture of ordinary gases, such as air and carbonic anhydride, hydrogen and sulphurous anhydride, was intermediate between that of each gas separately for the same variations of pressure (*ibid.*, 258).

The results of all experiments which had been carried out up to the time when the author's investigations were commenced, had been to show that, with one exception, Dalton's law is true in all cases for mixtures of gases or vapours, or at any rate in the case of gases and vapours which exert no chemical action on one another. A mixture of the vapours of two mutually soluble liquids, in presence of the two liquids mixed or dissolved, constitutes, however, an important exception to this law, because of the disturbing influence of the chemical affinity of the liquids. But as, up to this time, no experiments had been carried out to prove the truth of Dalton's law under pressures greater than 2 atmospheres, the author investigated the change in volume of a mixture of 3 vols. of pure carbonic anhydride and 4·05 vols. of nitrogen at temperatures above and below the critical temperature of carbonic anhydride, the pressure employed varying between about 40 and 300 atmospheres.

From the results, which are given in tabular form, curves are drawn showing the volume of the mixture at the various temperatures and pressures. These curves are all very similar, showing no difference in character for temperatures above or below 31°. If it be granted that Dalton's and Boyle's laws are true in the case of nitrogen under the pressures employed, the curves showing the change in volume of the carbonic anhydride in the mixture under the various conditions of temperature and pressure prove that below 31° this gas tends to occupy the volume corresponding with the liquid state, although the curves are quite different from those of carbonic anhydride alone. It follows, therefore, that Dalton's law is no longer applicable in this case, and is only strictly true of a perfect gas.

As no liquefaction took place in any of the above experiments, showing that the presence of nitrogen lowered the critical point of the carbonic anhydride, the author investigated this phenomenon more fully. A mixture of 6·2 vols. of carbonic anhydride and 1 vol. of nitrogen was placed under a pressure of 48·3 atmospheres; no condensation occurred until the temperature was lowered to 3·5°. As the pressure was increased the volume of the liquid augmented, and after each increase of pressure, the volume continued to augment slowly for some time; for example, under a pressure of 82 atmospheres the relative volumes of the gas and liquid were at first 8·5 and 5·8, but, the apparatus having been left for some time, the volume of the liquid slowly increased. The pressure having been then raised to 102 atmospheres, the volume of the gas which was at first 1·7 diminished gradually until only a small globule remained, which finally disappeared entirely, the nitrogen dissolving in the liquid carbonic anhydride. In a second experiment, with the same mixture at a higher and constant temperature, the liquid had at first its usual concave surface, and as the pressure was increased, the volume of the liquid also augmented without any noticeable change in the appearance of the concave surface; on further increasing the pressure, the surface of separation appeared in section as a fine line, but when the pressure was again increased, it disappeared entirely, the whole becoming homogeneous. The position in the tube, occupied by the surface of separation, depended on the temperature at which the observation was made; at 14° the liquid filled about two-thirds of the entire space at the very moment when the surface of separation was about to disappear.

The critical temperature of a mixture of 1 vol. of nitrogen and 3·43 vols. of carbonic anhydride was found to be 14°, and the corresponding pressure 98 atmospheres. Experiments with this mixture showed that at 6·3° no condensation took place until the pressure reached 68·7 atmospheres; the liquid then disappeared under increased pressure, but reappeared when the pressure reached 113·2 atmospheres. At 9·9°, the liquid first appeared when the pressure reached 77·6 atmospheres; after having disappeared it was again formed under a pressure of 107·8 atmospheres. At 13·2°, the liquid appeared under a pressure of 91·6 atmospheres, disappeared as the pressure was increased, and reappeared when it attained 103·2 atmospheres. If the mean of the two pressures for each of the above temperatures is taken, the critical pressure at 6·3°, 9·9°, 13·2°, and 14° is found to be 90·9, 92·7, 94·4, and 98 atmospheres respectively.

In the course of these experiments, the author found it convenient to employ a tube bent twice at right angles. When the gaseous mixture was compressed below the critical point, the liquid carbonic anhydride collected in the lower portion of the tube, although part of the liquid was first formed at the surface of the mercury; but the whole of the liquid soon collected at the bottom of the tube. In some experiments, the carbonic anhydride liquefied at temperatures above 20°, and sometimes no condensation took place even a few degrees below this temperature. This phenomenon was found to be owing to the fact that when liquefaction had taken place, if the pressure was diminished so that the mixture could become completely gaseous, the liquid separated into two portions, one rich, the other poor, in carbonic anhydride. The portions of the tube which had been previously occupied by the liquid then contained a large excess of carbonic anhydride, especially when the tube had been previously cooled to −10°, so that almost the whole of the carbonic anhydride had been liquefied. If the pressure was reduced so as to bring the whole of the liquid to the gaseous state, the temperature being at the same time raised to 26°, it was found that the carbonic anhydride could be liquefied by pressure alone (at 26°), provided that the experiment was performed without loss of time. When, however, the mixture was left for some time in the gaseous state, diffusion gradually took place, and the temperature at which liquefaction was possible decreased accordingly. Diffusion was not complete until after some hours, and then increased pressure caused no liquefaction until the temperature was reduced to 14°.

This method of separating the gases was employed to show the effect of diffusion as follows:—A mixture of carbonic anhydride and nitrogen was kept at 8·5° under a pressure of 46·4 atmospheres until diffusion was complete; the volume of the mixture was then 162·2. After liquefying the carbonic anhydride by employing great pressure and lowering the temperature to −12°, the temperature was again raised to 8·5°, and the pressure brought back to 46·4 atmospheres; the volume was then found to be 159·5, showing that a contraction of 2·7 vols. had taken place owing to the separation of the mixed gases. At the end of 1½ hours the volume had increased to 161·5 in consequence of partial diffusion.

In a second experiment at 16°, under a pressure of 47·9 atmospheres, the original volume of the mixture was 164·6, but, after liquefaction, only 161·9 when brought back to the initial temperature and pressure; after 1½ hours the volume had increased to 164·1. In a third experiment at 20°, under a pressure of 46·4 atmospheres, the volume decreased from 175·8 to 173·5 after the separation of the gases.

These results show that when the two gases diffuse into one another under great pressure, an increase in volume occurs, and when they are separated the volume is diminished. This change in volume undoubtedly occurs also under ordinary pressures, but the variation would probably be so small that it would be difficult to detect experimentally. F. S. K.

The Behaviour in Relation to Boyle's Law of certain Gases at Low Pressures. By F. Fuchs (*Ann. Phys. Chem.* [2], **35**, 430—450).—The author, from the results of a series of experiments on atmospheric air, carbonic and sulphurous anhydrides and hydrogen, arrives at the following conclusions:—

(1.) At ordinary temperatures, Boyle's law does not represent a limiting state towards which a gas approaches indefinitely with increasing rarefaction, but at pressures respectively above and below a certain amount, the deviations from Boyle's law are respectively positive and negative. The limits of pressure within which Boyle's law holds are indefinitely small, as any finite change in volume will alter the forces between the gaseous molecules.

(2.) In the case of atmospheric air at the temperature 0°, a change of sign of this kind takes place at a pressure very slightly below the ordinary atmospheric pressure. If any similar change of sign occurs with carbonic and sulphurous anhydrides, it must be at pressures less than any at which the author's observations were made.

(3.) The deviations from Boyle's law in the case of hydrogen at low pressures are so small that hydrogen under these circumstances may, without sensible error, be regarded as a perfect gas.

G. W. T.

Constitution of Solutions. By F. Rüdorff (*Ber.*, **21**, 3044—3050).—Salts of the composition $R_2SO_4 + R''SO_4 + 6H_2O$ and $R_2SO_4 + R_2'''(SO_4)_3 + 24H_2O$ are partially decomposed into their constituents when dissolved in water (compare Abstr., 1888, 342). Hydrogen potassium sulphate behaves similarly, but hydrogen ethyl sulphate diffuses unchanged. The following salts:—

$$3K_2C_2O_4,Fe_2(C_2O_4)_3 + 6H_2O;\ 3Na_2C_2O_4,Fe_2(C_2O_4)_3 + 6H_2O;$$
$$3K_2C_2O_4,Cr_2(C_2O_4)_3 + 6H_2O;\ 2(NH_4)HC_2O_4 + H_2O;$$
$$NaHC_4H_4O_6 + H_2O, \text{ and } 2K(SbO)C_4H_4O_6 + H_2O,$$

diffuse unchanged, but $(NH_4)HC_2O_4,C_2H_2O_4 + 2H_2O$ is partially decomposed into oxalic acid and hydrogen ammonium oxalate.

Solutions of potassium chromate, potassium dichromate, and sodium dichromate diffuse unchanged, but the salt

$$(NH_4)_2CrO_4,MgCrO_4 + 6H_2O$$

is partially decomposed when dissolved in water.

The following salts:—$2NaCl,PtCl_4 + 8H_2O$; $2KCl,PtCl_2$; $2NH_4Cl,HgCl_2$; $Ba(CN)_2,Pt(CN)_2 + 4H_2O$, and all double cyanides are true molecular compounds, but $KCl,Hg(CN)_2$ is partially resolved into its constituents when dissolved in water (*loc. cit.*). NaH_2PO_4 and Na_2HPO_4 diffuse unchanged: Na_3PO_4, on the contrary, is partially decomposed. The three sodium salts of citric acid are not decomposed in aqueous solution.

F. S. K.

Physical Properties of Colloïd Solutions. By C. Lüdeking (*Ann. Phys. Chem.* [2], **35**, 552—557).—In a paper with Wiedemann (Abstr., 1885, 1031) it was shown that the vapour-pressure of a

40 per cent. aqueous solution of gelatin was less at a temperature of 40° than that of pure water. According to Guthrie (this Journal, 1877, i, 36), a 40 per cent. solution of gum boiled at 98°, and a 45 per cent. solution of gelatin at 97·5°: results which were in contradiction to those above mentioned.

With a view of discovering the reason of the discrepancy, the author made experiments on solutions of gum arabic, gum tragacanth, dextrin, starch, and agar-agar.

He finds that a 40 per cent. solution of gum arabic boils at 100°, but carbonic anhydride begins to be given off at a temperature of about 90°, and at a somewhat higher temperature gives the appearance of boiling to the solution.

The other solutions also boiled at 100°, although in the case of gelatin boiling began with the thermometer at 98°, which, however, the author attributes to the liquid not rapidly assuming the same temperature throughout, owing to its viscidity preventing the formation of convection currents. This opinion was based on the fact that the thermometer did not remain at 98°, but gradually rose to 99·8°, where it remained constant.

The author found that the addition of the colloïd in every case slightly lowered the vapour-pressure, and, as he points out, the presence of a solid in solution could not possibly increase the vapour-pressure. For example, if the steam given off at 98° from a gelatin solution had a pressure of 760 mm., it would necessarily recondense to water and mix again with the solution.

When solutions of gum or gelatin are cooled considerably below zero, the author finds that they do not solidify as a whole, as stated by Guthrie, but ice crystals gradually separate out. He finds that gelatin has a strong condensing action on the water of solution.

G. W. T.

Precipitation of Colloïd Substances by Salts. By O. NASSE (*Pflüger's Archiv*, **41**, 504—514).—All proteïds except peptone can be precipitated by saturating a neutral solution with ammonium sulphate, some more easily than others, for instance, globulins more easily than albumins. Other salts have the same power, but none act so readily as ammonium sulphate. This property, however, is not characteristic of proteïds: soaps, gelatin, and certain soluble carbohydrates (glycogen, amidulin, inulin, &c.), are similarly precipitated; it in fact seems to be a property common to colloïd substances.

The question arises, on what does the difference in the concentration of the salt necessary to produce precipitation depend? Is the action of the salt simply due to a struggle of the molecule of proteïd, gelatin, &c., with that of the salt for water, and that the precipitation of the colloïd substance occurs as soon as its water-attracting power is exceeded by that of the salt?

In order to determine whether this is the case, one must ascertain the amount of two or more different salts necessary to precipitate the same amount of one colloïd substance, the necessary concentration of the salt solutions corresponding with $a : b : c$, &c. The same question is then investigated for another colloïd substance, and the ratio

$a' : b' : c'$, &c., found. If then we have only to deal with attraction for water, $a : b : c$, &c., will be found $= a' : b' : c'$, &c.

The following table illustrates the results obtained:—

	The solution contained in 100 c.c. the following amounts of salt when precipitation began.		
Colloïd substances.	*a.* Ammonium sulphate.	*b.* Magnesium sulphate.	*a* : *b*.
Gelatin	12·4	14·8	0·84
White of egg......	20·2	19·6	1·03
"	18·5	19·3	0·95
Serum proteïds	17·4	18·5	0·94
Albumose.........	12·7	13·6	0·93
"	14·9	17·6	0·85
Amidulin.........	20·9	10·5	1·99
Glycogen-dextrin ..	44·7	22·7	1·99

The differences of the numbers in the last column show that water-attracting power is not the only influence at work, but some other relation must exist between the colloïd and the salt. Still it is possible that it may explain some of the precipitations, especially that of gelatin. Gelatin loses many of its characteristic properties after the prolonged heating of its solutions; it, for instance, no longer gelatinises on cooling, and its water-holding power is greatly increased, yet the ratio $a : b = 0·84$ remains constant for the gelatin in all the different stages of this change.

With regard to the proteïds, in which such wide differences occur, it is thought probable that the explanation lies in the fact that loose compounds with the salts are formed.

The paper concludes with some remarks on the influence of temperature in determining precipitation by salts. W. D. H.

New Formula for Calculating the Molecular Volumes of Chemical Compounds at the Boiling Points. By J. A. GROSHANS (*Rec. Trav. Chim.*, 7, 220—225).—The molecular volume of a substance, $C_pH_qO_r$, at the boiling point may be represented by $v_s = a + 10(p + q) - 7·28\,B$ for a fatty compound, or by the same expression *minus* 15 for an aromatic compound, a being the number of c.c. equal to the molecular weight of the compound, and $B = p + q + r$. Both these formulæ obey Kopp's rules, that homologous compounds differing in their composition by CH_2 should differ in their molecular volumes by 22, and that a fatty compound should have approximately the same volume as an aromatic compound which differs in its formula by $C_2 - H_4$.

With hydrocarbons, since $r = 0$, the formula may also be written $(v_s - a)/B = 2·72$ for fatty compounds, or $(v_s - a + 15)/B = 2·72$ for aromatic, both of which are found to agree well with experiment. For halogen-derivatives, an addition of 15 must be made for each atom of halogen contained. H. C.

Molecular Lowering of the Freezing Point of Benzene by Phenols. By E. PATERNÒ (*Ber.*, **21**, 3178—3180).—The author made a number of experiments to ascertain whether the fact that certain substances containing the hydroxyl-group produce an abnormal lowering of the freezing point of benzene was true of all substances, and whether this abnormal behaviour was sufficient proof of the presence of the hydroxyl-group (compare Raoult, Abstr., 1884, 953). The results showed that although phenol behaves in an abnormal manner, the following compounds: ethylphenol, acetylphenol, two isomeric nitrophenols, tribromophenol, picric acid, paracresol, methyl salicylate, thymol, nitrothymol, nitrosothymol, α-naphthol, β-naphthol, and benzylphenol, all produce the normal lowering of the freezing point of benzene and of acetic acid, either in dilute or moderately concentrated solutions, the variations caused by change in concentration of course being taken into consideration.

The molecular weight of water determined by Raoult's method in acetic acid solution was found to be 18 (compare Raoult, *loc. cit.*), but the author points out that this result is not by any means conclusive, as, even if the molecules were originally more complex, they would be simplified by the act of solution.

Hentschel's experiments with acetic acid (*Zeit. phys. Chem.*, **2**, 308) seem to point to an opposite conclusion, but in this case the freezing point of the benzene solution was considerably below that of acetic acid. The fact that the molecular weight of water is found to be 36 when the freezing point of the solution lies below 0° shows that the temperature at which the mixture freezes is a most important factor in the case. F. S. K.

Inorganic Chemistry.

Preparation of Chemically Pure Hydrogen Peroxide. By MANN (*Chem. Zeit.*, **12**, 857).—Hydrogen peroxide of commerce contains many impurities; it is mixed with a ¼ per cent. of phosphoric acid and then, while stirring vigorously, barium hydroxide is added until the solution is exactly neutral to litmus. The clear solution is poured into a cold saturated solution of barium hydroxide, and the precipitate of barium peroxide is well washed and may be kept for the preparation of pure hydrogen peroxide. For this purpose, it is made into a thin magma and carefully decomposed by dropping steadily into dilute sulphuric acid containing 12 per cent. of concentrated acid; any excess of sulphuric acid being removed by hydroxide, and *vice versâ*. Excess of barium peroxide must be avoided as it decomposes hydrogen peroxide. D. A. L.

Compounds of Chlorine with Iodine. By W. STORTENBEKER (*Rec. Trav. Chim.*, 7, 152—205).—The only compounds of iodine with chlorine which are capable of existing in the solid state are ICl and ICl_3. Two modifications of the first exist which the author terms α and β. ICl is best prepared by passing dry chlorine over iodine and then distilling the product with a few grams of iodine. If the distillate is allowed to solidify at −25°, the α-modification is obtained in long, dark-red needles, melting at 27·2°. If the crystallisation take place between +5° and −10°, modification β is usually, but not invariably, obtained. When slowly formed, it crystallises in dark-red plates melting at 13·9°. It is unstable and readily converted into the α-modification, into which it is gradually changed. The most favourable temperatures for its existence are between 0° and −10°. If cooled below −12° it changes into the α-modification.

The trichloride ICl_3 is prepared by treating iodine, or the liquid ICl with excess of chlorine. It sublimes very readily and settles on the sides of the apparatus in slender, yellow needles. It melts at the ordinary pressure at temperatures varying between 20° and 60°, but under a pressure of 16 atmos. melts regularly at 101°. After fusion, it solidifies in brownish-red crystals.

The author further shows that every mixture of the two elements, chlorine and iodine, is possible in the liquid state above a certain temperature which depends on the proportion of the two elements. Below that temperature, one of the substances I_2, $ICl\alpha$, $ICl\beta$, ICl_3, or Cl_2 will separate in the solid state. If on a diagram representing pressures and temperatures the two points be taken at which chlorine and iodine melt, corresponding with the temperatures −102° and 114·3°, then between these points will lie the curve which is the locus of the points at which the various mixtures of chlorine and iodine exist in the liquid state. These two end points are triple points for the pure elements, and on the intermediate curve will be found three quadruple points, each corresponding to equilibrium between four phases (comp. Roozeboom, Abstr., 1888, 1151).

t.	*p.*	Phases present.
7·9°	11 mm.	I_2, $ICl\alpha$, $I \sim Cl_{0\cdot66}$, $I + Cl_{0\cdot02}$ (gas).
22·7	42 ,,	$Cl\alpha$, ICl_3, $I \sim Cl_{1\cdot19}$, $I + Cl_{1\cdot75}$ (gas).
−102·0	< 1 atmos.	ICl_3, Cl_2, $I \sim Cl_n$, $I + Cl_m$ (gas).

Complete solidification will only occur at the three distinct temperatures of the quadruple points, when separation of a mixture of the solids $I_2 + ICl$, $ICl + ICl_3$ or $ICl_3 + Cl_2$ will take place.

A study of the compounds of iodine and chlorine in the gaseous state shows that molecules ICl exist in that condition, and only suffer slight dissociation even at 80°, whereas ICl_3 cannot exist as gas, the molecules undergoing complete dissociation. H. C.

Theory of the Lead Chamber Process. By F. RASCHIG (*Annalen*, **248**, 123—140), and by G. LUNGE (*Ber.*, **21**, 3223—3240).—Controversial papers.

Compounds of Ammonia with Selenious Anhydride. By C. A. CAMERON and J. MACALLAN (*Proc. Roy. Soc.*, **44**, 112—115).—Dry ammonia passed into an alcoholic solution of selenious anhydride forms *ammonium selenosamate*, $NH_4{\cdot}SeO_2{\cdot}NH_2$, which crystallises in hexagonal prisms and pyramids. It loses ammonia very easily even on exposure to air or treatment with solvents and on heating. It is only partially converted into ammonium selenate by the action of water even after continued boiling. Potassium hydroxide at once liberates ammonia. Sulphuric acid reacts violently with it, and chlorine oxidises it to ammonium selenate. Sulphurous anhydride and stannous chloride reduce it with separation of selenium. The acid salt formed from the above by loss of ammonia has the composition $(NH_4)H(SeO_2{\cdot}NH_2)_2$, and is a deliquescent salt soluble in alcohol. It behaves like the normal salt, but is much more stable. When strongly heated, it is decomposed into ammonium selenite, ammonia, water, nitrogen and fused selenium. These compounds of selenious anhydride are more akin to the compounds of sulphuric anhydride with ammonia than to those of sulphurous anhydride. H. K. T.

Constitution of Phosphorous Acid. By V. WEDENSKY (*J. Russ. Chem. Soc.*, 1888, **20**, 29—32).—When phosphorous acid is dissolved in acetic anhydride, a colourless crystalline substance separates after a time. This is washed with ether and analysed; the results agree with the formula of a monacetyl-derivative of phosphorous acid, $(C_2H_3O)H_2PO_3$. When acetic anhydride acts on phosphorus trichloride, an analogous compound is obtained; this, however, seems to be a mixture, and cannot be obtained free from chlorine. A phosphorous triacetyl-derivative could not be obtained.

B. B.

Compounds of Arsenious Acid with Sodium Iodide and Bromide. By F. RÜDORFF (*Ber.*, **21**, 3051—3053).—The compound $NaBr,2As_2O_3$ is obtained when arsenious acid (20 grams) and sodium bromide (120 grams) are dissolved in boiling water (350 c.c.), and the filtered solution allowed to cool slowly (compare Abstr., 1887, 107). It crystallises in hexagonal plates and is decomposed when warmed with water.

The compound $NaI,2As_2O_3$, prepared by dissolving arsenious acid (22 grams) and sodium iodide (60 grams) in hot water (500 c.c.), crystallises in hexagonal plates and is decomposed by hot water.

F. S. K.

Preparation of Boron and Silicon by Electrolysis. By W. HAMPE (*Chem. Zeit.*, **12**, 841).—When fused borax is submitted to electrolysis in a gas-carbon crucible with a platinum positive and a gas-carbon negative electrode, oxygen is evolved from the platinum, whilst in the first instance sodium separates at the negative electrode, but this by a secondary reaction liberates boron. The negative electrode is from time to time withdrawn from the crucible, and when cool, the slag carrying the boron is carefully knocked off. This is treated with hydrochloric acid and water, leaving pure amorphous boron mixed with a small quantity of carbon and some isolated microscopic crystals of, at present, unknown composition. Fused boric anhydride does not conduct. But amorphous silicon may be prepared in a similar manner from fused sodium silicate.

D. A. L.

Beryllium Silicates. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **107**, 786—789).—If the constituents of an aluminium or beryllium leucite are fused at 600—800° with excess of potassium vanadate, mineralisation takes place rapidly, but the composition of the product varies as the vanadate gives up more or less of its alkali, and it is rarely homogeneous. The product is washed with water and very dilute potash, and the crystalline constituents are separated by solutions of cadmium tungstoborate of varying specific gravity.

All the products crystallise in icositetrahedrons, a^2. In the aluminium compounds, the potassium and aluminium are always present in the proportion $Al_2O_3 : K_2O$, whilst in the beryllium compounds the ratio of beryllia to potash varies from 1·25 to 0·5. The silicate containing $Be_2O_3,2K_2O$ is obtained with a mixture which always contains an excess of alkali, whilst the silicate containing Be_2O_3,K_2O is obtained with a neutral mixture. In the aluminium compounds, the ratio of silica to potash varies from 4 to 5, whilst in the beryllium compounds the same ratio varies from 4·5 to 5·0. In the latter case, the product is always heterogeneous, and probably results from the simultaneous crystallisation of silicates containing $4SiO_2$ and $5SiO_2$. The silicate $4SiO_2,Be_2O_3,K_2O$ is obtained in icositetrahedrons by rapidly heating its constituents to a high temperature and cooling very gradually.

Products were also obtained containing both alumina and beryllia. They are all fusible, and are homogeneous with respect to sp. gr. The following ratios were observed:—$K_2O : SiO_2 :: 1 : 4·5—4·8$; $K_2O : R_2O_3 :: 1 : 0·75—1·0$; $Be_2O_3 : Al_2O_3 :: 1 : 0·5—1·75$. Silicates containing beryllia and ferric oxide are yellowish, crystallise in the same form, and are homogeneous with respect to specific gravity. The following ratios were observed:—$K_2O : SiO_2 :: 1 : 4·59—5·0$; $K_2O : R_2O_3 :: 1 : 0·6—1·3$; $Be_2O_3 : Fe_2O_3 :: 1 : 0·3—1·3$.

Alumina and silica in the proportion of 1 mol. of Al_2O_3 to 6 mols. of SiO_3, heated with potassium vanadate, yield orthoclase in macled, prismatic crystals; but with beryllia in place of alumina, the crystals are always icositetrahedrons. With a mixture of alumina and beryllia, however, non-macled, prismatic crystals, of the composition $6SiO_2,R_2O_3,K_2O$ are obtained, and are homogeneous with respect to specific gravity. The ratio $SiO_2 : K_2O$ remains constant, whilst the ratio $Al_2O_3 : Be_2O_2$ varies.

The silicates obtained with beryllium may be regarded as mixtures of the following compounds:—

$8SiO_2,Be_2O_3,2K_2O$ $10SiO_2,Be_2O_3,2K_2O$,
$4SiO_2,Be_2O_3,K_2O$ $5SiO_2,Be_2O_3,K_2O$.

The fact that the beryllia can be replaced by alumina and ferric oxide in these compounds, and can replace alumina in orthoclase, combined with the well-known relations of beryllium to magnesium, would seem to indicate that beryllia has sometimes the functions of a monoxide and sometimes those of a sesquioxide. C. H. B.

Occlusion of Gas by Electrolytic Copper. By A. SORET (*Compt. rend.*, **107**, 733—734).—With dilute copper solutions, unless the current is very weak, the precipitated metal is spongy, the nature of the deposit depending not only on the strength of the solution and the intensity of the current, but also on the proportion of free acid present. Lenz obtained 4·4 vols. of hydrogen from 1 vol. of deposited copper.

The author finds that electrolytic copper always contains hydrogen, which, however, is simply occluded. There is a connection between the volume of gas occluded and the temperature and acidity of the solution. These conditions also affect the malleability of the metallic deposit. The occluded hydrogen sometimes contains small quantities of carbonic anhydride and traces of carbonic oxide. C. H. B.

Mechanical Properties of Metals in Relation to the Periodic Law. By W. C. ROBERTS-AUSTEN (*Proc. Roy. Soc.*, **43**, 425—428). —Very pure gold was alloyed with 0·2 per cent. of various metals, and the tensile strength determined. The tenacity was found to be affected by the elements in the order of their atomic volumes, those elements which have a higher atomic volume than gold diminishing its tenacity very considerably, whilst silver, which has nearly the same atomic volume as gold, hardly affects either its tenacity or extensibility. Hence it appears that Carnelley's law—that "the properties of compounds of the elements are a periodic function of their atomic weights," may also be applied to alloys. Tenacity was chosen for examination, since those metals which are most tenacious have the highest melting points, and the melting point, according to Pictet, is intimately connected with the lengths of the molecular oscillations. H. K. T.

Dissolution of Iron in Aqueous Soda. By G. ZIRNITÉ (*Chem. Zeit.*, **12**, 355).—When a strong current of air is blown into a hot, concentrated solution of soda containing about 34 per cent. of hydroxide, standing in an iron vessel, or to which finely divided hydrated ferric oxide has been added, perceptible quantities of iron are dissolved without colouring the liquid. The solution remains clear and colourless for several days at the ordinary temperature, but ultimately becomes turbid, yellow, and finally red, owing to the separation of the hydrated ferric oxide; this colour, however, disappears again on heating. When the colourless solution is diluted, the ferric oxide is precipitated in about half an hour, but is redissolved by concentrating the diluted solution. Hydrogen sulphide at first produces a deep, cherry-red coloration in the colourless liquid, and on continuing the action a greenish-black precipitate is formed, leaving a clear solution free from iron, but slightly yellow from sodium sulphide. It is suggested that the iron exists in solution as sodium perferrate, $NaFeO_4$. D. A. L.

Ammonium Fluoroxymolybdates. By F. MAURO (*Chem. Centr.*, 1888, 1056—1057, from *Mem. R. Acad. dei Lincei* [4], 4, 481—488).—*Triammonium fluoroxymolybdate*, $MoO_2F_2,3NH_4F$, prepared by evaporating a solution of ammonium molybdate in excess of ammonium fluoride solution acidified with hydrogen fluoride, is obtained in clear and colourless rhombic prisms. The faces (100), (010), (110), and (011) were observed, and the angles (100) : (110) = 28° 36′, (011) : $(0\bar{1}1)$ = 82° 29′, and (011) : (110) = 71° 36′. Axial ratio, $a : b : c = 0{\cdot}5452 : 1 : 0{\cdot}8767$. It is soluble in water, producing an acid solution. On heating, white fumes are evolved and anhydrous molybdic acid remains. It contains no water of crystallisation.

Fluorammonium-molybdic anhydride, $MoO_3,2NH_4F$, prepared by adding ammonia to the solution of the last-named salt, and is thus obtained as a white, microscopic, crystalline precipitate. Larger crystals may be obtained by dissolving the compound in a hot solution of ammonium fluoride and ammonia, and allowing to evaporate spontaneously by exposure to the air or over sulphuric acid, when the salt crystallises out—at first as prisms, but later in octahedrons. If the precipitated salt is simply dissolved in ammonia and then allowed to evaporate, monoclinic crystals of hydrated ammonium molybdate separate first, then, later, the prisms and octahedrons of the new salt. The crystals appear usually in the form of twins, grown together in such a manner as to give the crystal the appearance of a hexagonal prism. They are shining, transparent, light-yellow, and belong to the rhombic system; $a : b : c = 0{\cdot}57464 : 1 : 0{\cdot}67705$. The faces (010), (001), (110), and (011) were observed. Twinning plane (110). The angles measured were: (110) : $(1\bar{1}0)$ = 59° 46′; (010) : (110) = 60° 7′; (010) : (011) = 55° 54′; and (110) : (011) = 73° 47′. This salt is decomposed by water. It is anhydrous, and is decomposed on heating above 100°, molybdic acid remaining.

Normal ammonium fluoroxymolybdate, $MoO_2F_2,2NH_4F$, is prepared from the last-named salt by spontaneous evaporation of the aqueous solution, rendered acid with hydrogen fluoride. It consists of brightly shining, transparent, colourless plates or prisms belonging to the rhombic system; $a : b : c = 0{\cdot}8413 : 1 : 1{\cdot}0164$. The faces (010), (001), (011), (201), and (221) were observed. The angles measured were: (001) : (201) = 67° 31′; (001) : (011) = 45° 28′; (001) : (221) = 72° 26′; (201) : (011) = 74° 27′; (011) : (221) = 49° 31′; and (201) : (221) = 37° 52′. This salt is sparingly soluble in water, and is decomposed by heating above 100°; ammonium fluoride and hydrogen fluoride are evolved, leaving molybdic acid.

Octahedric ammonium fluoroxymolybdate,

$$MoO_2F_2,4NH_4F,(NH_4)_2MoO_4,$$

a double salt of ammonium fluoroxymolybdate with ammonium molybdate, is prepared by allowing a solution of triammonium fluoroxymolybdate in ammonia to evaporate spontaneously in the air or over sulphuric acid. It forms small, colourless, transparent, lustrous octahedrons, which gradually disintegrate when exposed to the air. It is isomorphous with the corresponding double salt of tungsten. It is soluble in water, and does not again crystallise out of the solution. It suffers decomposition, like the other salts, when heated above 100°.

Ammonium dimolybdate, $2MoO_3,(NH_4)_2O + H_2O$, prepared by dissolving fluorammonium-molybdic anhydride in ammonia and allowing the solution to remain. It forms transparent, colourless, lustrous, monoclinic crystals—usually pyramidal;

$$a : b : c = 0{\cdot}99628 : 1 : 0{\cdot}94497 ; \beta = 72° 47' 41''.$$

The faces observed were: (100), (010), (011), $(10\bar{1})$, (111), and $(\bar{1}11)$; the angles: (001) : (100) = 72° 48'; (001) : $(\bar{1}01)$ = 52° 44'; (100) : $(10\bar{1})$ = 54° 28'. By heating above 100° this compound behaves exactly like the other members of the series, and leaves a residue of molybdic acid. J. W. L.

Tin. By L. VIGNON (*Compt. rend.*, **107**, 734—737).—When sheet zinc is immersed in a solution of a tin salt which contains no free acid, and the precipitated tin is washed with water and dried in contact with air, the product is infusible and burns like tinder when heated in presence of air. If heated to redness in a porcelain tube in a current of carbonic anhydride for two hours, it separates into small globules of fused tin and a grey powder. These are separated by levigation, and after the powder has been dried, it burns readily when heated in the air. The infusible tin occurs in slender, dendritic forms of sp. gr. 6·910 to 7·198 at —15°, and contains 96 to 97·3 per cent. of tin. It dissolves readily in hydrochloric acid with evolution of hydrogen. The alteration in the properties of the tin does not take place during precipitation, but when the tin is dried in contact with air it is partially converted into stannous oxide, the alteration taking place the more readily the less the proportion of free acid in the liquid from which the tin is precipitated. If much free acid is present, the tin does not oxidise when dried. The proportion of stannous oxide in the oxidised tin varies from 22·5 to 33·4 per cent., and when combustion takes place stannic oxide is formed.

C. H. B.

Fluorine-derivatives of Vanadium and its Analogues. By E. PETERSEN (*Ber.*, **21**, 3257—3259).—The following compounds were prepared by treating the oxides dissolved in hydrofluoric acid with a solution of the various fluorides.

(I.) *Compounds derived from the Sesquioxide.*—(1) $V_2F_6 + 6H_2O$, large, readily soluble, dark green rhombohedra; (2) $V_2F_6,4KF + 2H_2O$, bright green, sparingly soluble, crystalline powder; (3) $V_2F_6,6AmF$, small, grass-green, regular octahedra; (4) $Cr_2F_6,6AmF$ (Wagner, Abstr., 1886, 676), rather darker green octahedra; (5) $Ti_2F_6,6AmF$ (Piccini, *Compt. rend.*, **97**), small, red-violet octahedra; (6) $Al_2F_6,6AmF$, sparingly soluble, dazzling white, crystalline powder; (7) $V_2F_6,4AmF + 2H_2O$, emerald-green, rather large crystals, like octahedra, but polarising; (8) $V_2F_6,2AmF + 4H_2O$, darker green, lamellar aggregates; (9) $V_2F_6,5NaF + H_2O$, bright green, sparingly soluble, crystalline powder; (10) $V_2F_6,2CoF_2 + 14H_2O$, small, dark green, monoclinic prisms; (11) $Cr_2F_6,2CoF_2 + 14H_2O$, pure dark green, monoclinic prisms; (12) $V_2F_6,2NiF_2 + 14H_2O$, grass-green, monoclinic prisms;

(13) $Cr_2F_6,2NiF_2 + 14H_2O$, emerald-green, monoclinic prisms. The last four compounds are isomorphous.

(II.) *Compounds corresponding with Vanadium Dioxide.*—(14) $VOF_2,3AmF$, small, blue, almost regular octahedra, but polarising; (15) $VOF_2,2AmF + H_2O$ (Baker, Trans., 1878, 392), larger, dark blue prisms; (16) $4VOF_2,7AmF + 5H_2O$, still darker blue, lamellar aggregates; (17) $4VF_4,2AmF + xH_2O$, small, blue-green prisms, stable only in solutions, strongly acidified with hydrogen fluoride; (18) $3VOF_2,7KF$; (19) $VOF_2,2KF$; (20) $3VOF_2,8NaF + 2H_2O$. These three form bright blue, sparingly soluble, crystalline powders.

(III.) *Compounds derived from the Pentoxide.*—(21) $VOF_3,2KF$, colourless, crystalline powder; (22) $2VOF_3,3KF,HF$, white, lustrous prisms; (23) $VF_5,VOF_3,4KF$, colourless aggregates of very slender needles; (24) $VO_2F,2KF$, golden-yellow, lustrous, hexagonal prisms, (25) $2VO_2F,3KF$, bright yellow prisms; (26) $5VOF_3,9AmF,3HF$, colourless, dull lustrous prisms; (27) $VO_2F,3AmF$, larger, straw-coloured, probably rhombic crystals; (28) $4VO_2F,7AmF,HF$, white, lustrous aggregates; (29) $2Nb_2O_5,3KF + 5H_2O$, lustrous white, sparingly soluble, crystalline powder; (30) $Nb_2O_5,KF + 3H_2O$, colourless prisms. The compounds 14, 19, and 27 seem to be identical with those prepared by Piccini and Giorgis (*Atti d. R. Acc. dei Lincei*, 1888, 590, and *Gaz.*, **18**, 186).

The thermochemical relation of hydrogen fluoride to the sesquioxides of iron, chromium, and vanadium was determined. The following numbers were obtained for the heat of neutralisation in dilute aqueous solutions:—$(Fe_2O_6H_6,6HF + Aq) = 47500$ cal., $(Cr_2O_6H_6,6AF + Aq) = 50330$ cal., $(V_2O_6H_6,6HF + Aq) = 52240$ cal.

N. H. M.

Decomposition of Antimony Sulphide by Boiling Water. By W. Elbers (*Chem. Zeit.*, **12**, 355—356).—When antimonious sulphide is boiled with water, it is decomposed with the evolution of hydrogen sulphide and the formation of antimonious anhydride. In this way 0·05 gram of the sulphide was completely converted into the anhydride in 14 hours; the liquid then had a slightly alkaline reaction.

D. A. L.

Mineralogical Chemistry.

Native Platinum from Canada. By G. C. HOFFMAN (*Jahrb. f. Min.*, 1888, ii, Ref., 386, from *Geol. Surv. Can. Rep.*, 2, 5).—Native platinum has been found with gold in several rivers in British Columbia. From the bed of Granite Creek, a tributary of the Similkameen river, grains were obtained varying in diameter from 1 to 4 mm., and weighing altogether 18·266 grams. The material was separated into a magnetic (I) and a non-magnetic portion (II), the compositions of which were as follows:—

	Pt.	Pd.	Rh.	Ir.	Cu.	Fe.	OsIr.	Chromite.	Total.
I.	78·43	0·09	1·70	1·04	3·89	9·78	3·77	1·27	99·97
II.	68·19	0·26	3·10	1·21	3·09	7·87	14·62	1·95	100·29

The sp. gr. of the magnetic portion was 16·095, and that of the non-magnetic portion 17·01. B. H. B.

The Pyroxenites of Morbihan. By C. BARROIS (*Jahrb. f. Min.*, 1888, ii, Ref., 413—414, from *Ann. soc. géol. du Nord*, 15, 69—96).—The pyroxenites of Morbihan form beds 0·1 to 2 metres in thickness in gneiss and mica-schists of Archæan age. The main constituent of these rocks is a pale green augite of the following composition:—

SiO_2.	CaO.	MgO.	Fe_2O_3.	Al_2O_3.	Na_2O.	K_2O.	Total.
51·5	24·3	11·9	8·5	5·0	1·1	trace	102·3

The augite is accompanied by zircon, titanite, and apatite in small quantities, by garnet and idocrase in varying amounts, and by quartz grains associated with felspar. Irregular grains of orthoclase only occur in certain beds, and microcline is also of exceptional occurrence. A fibrous actinolite is, however, present in large quantities, in many cases replacing the augite, so that rocks resembling nephrite are produced. Titaniferous iron ore and ferric hydroxide are also present. By the variety of the character and relative proportions of the constituents, numerous distinct types are distinguished, which may occur in the same bed. The author regards these pyroxenites as metamorphic limestones. B. H. B.

Riebeckite, and the New Formation of Albite in Granitic Orthoclase. By A. SAUER (*Chem. Centr.*, 1888, 1128, from *Zeit. deut. geol. Gess.*, 40, 138—152).—A new member of the hornblende-granite group has been found by the author in Socotra. This hornblende, named *riebeckite*, has the same composition as arfvedsonite, and is the analogue of ägirin of the augite series. From the analysis (No. 1 below) the formula $5FeSiO_3,4Na_2SiO_3,5Fe_2Si_3O_9$ has been calculated.

The Socotra granite is much disintegrated, and the author was thus enabled to examine more completely certain interchanges in the granitic orthoclases. The microscopical examination showed an opalescence from the edge towards the centre of the crystals, occasioned by the formation of albite, the crystals having been originally perfectly clear and without inclosures. The following are the analyses of riebeckite (1) and the secondary albite (2):—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	MnO.	CaO.	Na_2O.	K_2O.
(1.)	50·01	—	28·30	9·87	0·34	0·63	1·32	8·79	0·72
(2.)	70·24	17·18	0·64	—	—	—	—	6·86	5·19

J. W. L.

The Dachberg, a Volcano of the Rhone. By F. RINNE (*Jahrb. f. Min.*, 1888, ii, Ref., 406—407, from *Jahrb. preuss. geol. Landesanst.*, 1886, 1—22).—Near Rasdorf on the Rhone is situated the Dachberg, on the summit of which is an unmistakeable crater. The unaltered basalt at the edge of the crater is a dense, glassy felspar-basalt, consisting of plagioclase, augite, olivine, magnetite, biotite, and apatite. The chemical composition of the basalt is as follows:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.
41·71	3·51	15·80	5·59	7·64	0·16	4·85	10·30	6·08

K_2O.	Li_2O.	SO_3.	Cl.	H_2O.	CO_2.	P_2O_5.	Total.	Sp. gr.
1·00	trace	0·12	0·46	2·22	2·01	trace	101·45	2·90

B. H. B.

Dolerite of Londorf. By A. STRENG (*Jahrb. f. Min.*, 1888, ii, Mem., 181—229).—The author has made an exhaustive mineralogical and chemical investigation of the typical dolerites of the Vogelsberg. The dolerite of Londorf, to which he has principally directed his attention, has the following percentage composition:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
49·08	1·82	13·43	6·49	5·92	8·92	9·58	1·00

Na_2O.	P_2O_5.	H_2O.	Total.
3·42	0·51	0·32	100·49

From analyses of its constituents, the dolerite is calculated to be composed of 1·18 per cent. of apatite, 56·01 per cent. of andesine, 19·80 per cent. of augite, 20·11 per cent. of olivine, and 3·10 per cent. of magnetite and titaniferous iron ore. B. H. B.

Porphyrites at Gabian. By P. DE ROUVILLE and A. DELAGE (*Compt. rend.*, **107**, 665—667).—Near Gabian in Hérault there is a dyke which runs north-east and south-west and consists of two porphyrites.

One of these, which is by far the more abundant of the two, cuts through silurian, devonian, and carboniferous beds without producing any noteworthy metamorphism, and then penetrates into coal-measures which have undergone somewhat profound alteration. It follows that this dyke was formed after the deposition of the coal-measures, and the fact that pebbles in the overlying permian conglomerate consist of the material of the dyke, shows that it was formed before the deposition of the permian beds. This dyke is not homogeneous: it contains apatite, zircon, magnetite, oligoclase, black mica, orthoclase, amorphous matter, chlorite, calcite, damourite, and quartz.

The second porphyrite forms isolated masses in the main dyke, and is of later formation than the lower permian, since the latter beds are somewhat altered where they come in contact with the dyke. It contains large crystals, the nature of which could not be determined, well developed and distinct microliths of labradorite, magnetite, augite which has to a great extent been converted into chlorite, calcite, chlorite, damourite, quartz, and ferruginous products of decomposition.

C. H. B.

Composition of the Serpentine Rocks of Colle di Cassimoreno and Monte Ragola. By C. MONTEMARTINI (*Gazzetta*, **18**, 103—112).—At Colle di Cassimoreno and also in the neighbourhood of Monte Ragola, Chistoni found isolated masses of serpentine rock exhibiting strong magnetic polarity. The author is indebted to him for the two specimens he has examined.

The serpentine of Colle di Cassimoreno is massive and compact; of brecciated and porphyritic appearance, with lustrous, lamellar crystals of enstatite (bronzite) disseminated through the dark-green ground-mass. Besides these crystals, diopside and picotite also occur, together with magnetite, which forms one of the principal constituents of the rock. The hardness of the ground-mass is 6·5 and the sp. gr. at 13° varies from 2·73 to 2·76.

The powdered rock is ash-grey in colour, and like all serpentine rocks has a marked alkaline reaction. Heated in contact with the air, it assumes an ochreous tint. It is partly decomposed by the action of hydrochloric or sulphuric acid, with separation of gelatinous silica; the unattacked portion consists principally of the crystals of enstatite and picotite. The rock on analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Loss on ignition.	Total.
41·19	2·77	4·03	4·33	2·32	34·03	10·13	98·8

The enstatite, separated as far as possible from the other constituents of the rock, was analysed, and the results are given under I. In II the composition of the lherzolite from Germagnano in Piedmont is given for comparison:—

	SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I.	50·65	5·05	7·99	1·68	31·44	2·78	99·59
II.	52·19	2·15	8·85	2·96	31·84	1·77	99·76

These results show that the enstatite is bronzite.

The rock therefore consists of a serpentine formed by the decomposition of peridote together with enstatite, diopside, magnetite, and other minerals; this is also borne out by the microscopical and optical examination, full details of which are given. The rock also contains olivine, diallage, and amphibole.

The sample of rock from Monte Ragola, which was from the rock mass of the mountain itself, had no magnetic polarity, and was quite different in appearance from the one just described.

The ground-mass is light-green with dull-green nodules disseminated in it; these can easily be separated, and on examination were found to consist of altered bastite. A microscopical examination showed that the rock had all the characters of a serpentine formed by the alteration of a pyroxenic mineral. Neither the enstatite, diopside, nor spinelle which characterise the Cassimoreno serpentine could be discovered in it. Its sp. gr. at 14° is 2·54.

The analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Loss on ignition.	Total.
39·18	3·65	7·26	1·55	0·42	34·79	12·81	99·66

Chromium, nickel, and manganese were also detected.

C. E. G.

Organic Chemistry.

Action of Zinc Ethide on Nitroethane. By I. Bevad (*J. Russ. Chem. Soc.*, 1888, **20**, 125—135).—The object of this investigation was to decide whether "nitroethane" is really a nitro-compound (V. Meyer), a hydroxylamine-derivative, $CH_3\cdot CO\cdot NH_2O$ (Kissel), or an isonitroso-derivative, $HO\cdot CH_2\cdot CH\colon N\cdot OH$ (Alexéeff). When zinc ethide, ether, and nitroethane are mixed in an atmosphere of carbonic anhydride, the mixture becomes red, and after some time crystals are formed which disappear again in about a fortnight. On decomposing the product of reaction with water, distilling, and treating the distillate with hydrochloric acid, a solution is obtained which on evaporation gives crystals of a very hygroscopic salt. On decomposing this with alkalis, a colourless oil of sp. gr. 0·8935 at 0° is obtained, which proved to be *triethylhydroxylamine*, Et_3NO. It is somewhat soluble in water and soluble in all proportions in ether, alcohol, and benzene. Its compounds with hydrochloric, sulphuric, and acetic acids are extremely hygroscopic. The oxalate, $(Et_3NO)_2,H_2C_2O_4$, was obtained by mixing ethereal solutions of its constituents. Triethylhydroxylamine and its salts have powerful reducing properties, as shown by their behaviour with silver, cupric, and mercuric salts. The original ethereal distillate contains in addition, some unchanged nitroethane, but no other product is formed, if the substances employed are in molecular proportion.

The author concludes that nitroethane is a true nitro-compound. Its reaction with zinc ethide takes place in different stages. At first crystals are formed of the formula $2EtNO_2 + 7ZnEt_2$ (as shown by zinc determinations). When these crystals disappear, the compound $Et_3N(OZnEt)_2$ is formed; and this reacts with water as follows: $Et_3N(OZn{\cdot}C_2H_5)_2 + 4H_2O = Et_3N(OH)_2 + 2C_2H_6 + 2Zn(OH)_2$. The $Et_3N(OH)_2$ being unstable, however, is converted into the free base with elimination of water.

Nitromethane treated in the same way with zinc ethide gives methyldiethylhydroxylamine. When zinc ethide is added to bromonitroethane, a violent reaction takes place, and when this is over, if the product is distilled with water, secondary nitrobutane, $CHMeEt{\cdot}NO_2$, boiling at 138°, is formed. In this way from lower nitro-compounds those of higher homologues may be formed by synthesis. Nitrobenzene with zinc ethide gives no higher nitro-compound, reduction taking place with formation of aniline. If nitroethane were acethydroxamic acid, it should be formed from hydroxylamine hydrochloride and acetic anhydride; the experiments, however, made by the author with this object, gave a negative result. B. B.

Action of Chlorine on Isopropylethylene. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 141—148).—Isopropylethylene (b. p. 21—22°) was brought in contact with chlorine by passing the gas into the vessel by means of a tube terminating at some distance from the surface of the liquid, in order to prevent the action from being too violent, and to keep the course of the reaction as uniform as possible from the beginning to the end. When no more drops were formed on the sides of the vessel, the process was stopped. Various temperatures from $-20°$ to $+16°$ were employed, but in all cases the products were the same. After washing and drying the product, a liquid was obtained which, when submitted to fractional distillation, boiled chiefly between 143° and 145°. A small part boiling at 100—143° was proved to be a monochloride. The principal portion boiling at 143—145°, was an additive product of isopropylethylene, $C_5H_{10}Cl_2$. Its sp. gr. at 0° is 1·1106 and 1·0923 at 17·5°. When heated in sealed tubes with fused potassium acetate and acetic acid at 120°, it is converted into a glycol; this boils at 212—219°; the quantity obtained, however, was so small, that no experiments could be made to prove that it was isopropylethylene glycol. Isopropylethylene, when acted on by alcoholic potash, yields a monochloro-derivative boiling between 91° and 96°. These experiments show that isopropyethylene and chlorine yield additive products only, as pointed out by Lwoff.

B. B.

Polymeride of Methyl Cyanide. By R. HOLTZWART (*J. pr. Chem.* [2], **38**, 343—344).—When an ethereal solution of methyl cyanide is acted on by sodium, a white powder is formed and methane is evolved; when treated with water, the powder yields a yellow oil which can be crystallised in white needles from a mixture of ether

and light petroleum. A better yield is obtained by digesting the powder with aqueous ether. The crystals melt at 52—53°, are soluble in ether, alcohol, benzene, and chloroform, sparingly so in water and light petroleum. The molecular formula is $C_4H_6N_2$. When digested with water, ammonia is evolved, and a crystalline precipitate, sparingly soluble in cold water, is formed, having the composition $C_8H_8N_2O$; and when treated with acetic chloride in ethereal solution, a yellow, amorphous precipitate of the composition $2C_4H_6N_2,COMeCl$ separates; this is decomposed by water, forming a white, crystalline powder of the formula $C_8H_9N_3$. The investigation is still in progress.
A. G. B.

Polymeride of Ethyl Cyanide. By E. v. MEYER (*J. pr. Chem.* [2], **38**, 336—343).—The white powder obtained by the action of sodium on ethyl cyanide (Abstr., 1888, 802) has been proved to be formed as follows:—(1) $Na_2 + 2EtCN = NaCN + C_2H_6 + C_2H_4Na{\cdot}CN$; (2) $C_2H_4Na{\cdot}CN + EtCN = C_6H_9NaN_2$. The oil which it yields on treatment with water crystallises in tables which melt at 47—48°, boil at 257—258° (uncorr.), are little soluble in cold water, decomposed by warm water, and soluble in ether and alcohol; the molecular formula $C_6H_{10}N_2$ has been obtained both by Raoult's method and by the vapour-density determination; when heated at 330—340° for several hours it is converted into ethyl cyanide. Hydrochloric acid decomposes it, half the nitrogen appearing as ammonium chloride and half as an oil soluble in ether; the ethereal solution is shaken with sodium hydroxide, dried over lime, and the pure oil precipitated by adding water. This oil has the composition C_6H_9NO, and is reconverted into the original substance when heated with strong ammonia. It would thus appear that the polymeride is *α-imidopropionylethyl cyanide*, $NH{:}CEt{\cdot}CHMe{\cdot}CN$, and the oil *α-propionylethyl cyanide*, or cyanodiethyl ketone, $COEt{\cdot}CHMe{\cdot}CN$. The former is converted into ammonia, carbonic anhydride, and diethyl ketone, when heated with strong hydrochloric acid at 150°, and the latter into propionic acid and ammonia when heated with aqueous potash. The imido-compound is converted into propylamine by reduction.
A. G. B.

Ammeline. By A. SMOLKA and A. FRIEDREICH (*Monatsh.*, **9**, 701—707).—When dicyanodiamide (1·5 grams) and carbamide (1·08 grams) are heated at 170—180° for 2½ hours, much ammonia is set free, and on treating the product with water an insoluble white residue remains, from which ammeline, $C_3H_5N_5O$ (yield 1·57 grams), may be obtained by dissolving it in alkali and reprecipitating with acetic acid repeatedly; finally recrystallising it from a hot aqueous solution of potash.

Ammeline can also be prepared by heating dicyanodiamide with cyanic or cyanuric acid. It may therefore be represented by one of the two formulæ, $N{:}C{\cdot}NH{\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}NH_2$ or

$$CO{:}N{\cdot}C(NH){\cdot}NH{\cdot}C(NH){\cdot}NH_2.$$

The authors consider that the first of these most probably represents the constitution of the compound, since ammeline, unlike biguanide-derivatives, of which the second formula represents a member, is not a strong base, and does not give coloured compounds with salts of cobalt and copper. G. T. M.

Sulphines and the Valency of Sulphur. By R. NASINI and A. SCALA (*Gazzetta*, **18**, 62—72).—The authors have been occupied for some time with the examination of organic sulphur compounds, especially with the object of proving the tetravalency of sulphur, and the appearance of Klinger and Maassen's work (Abstr., 1888, 357), whose results are diametrically opposed to theirs, compels them to publish a portion of their researches. Although various sulphur compounds containing alkyl radicles have been obtained, of the form SM_3A and $SM_2M_{,}A$, unfortunately their vapour-density cannot be determined, and it remains uncertain therefore whether the four monad radicles are united to the sulphur, or whether the compounds are molecular compounds.

Klinger and Maassen, in repeating Krüger's work, found that the sulphine containing one methyl- and two ethyl-groups was the same, whether it was prepared by the action of methyl iodide on ethyl sulphide or of ethyl iodide on ethyl methyl sulphide, that is, they denied Krüger's statement that two isomeric compounds of the formula Et_2MeS existed, capable of yielding distinct platinochlorides crystallising in different forms. Nasini and Scala state that they have prepared the iodides of the sulphine according to Krüger's directions, and converted them into the corresponding platinochlorides, one of which crystallises in the cubic system, whilst the other is monoclinic.

Ethylmethylethylsulphine platinochloride, $(EtMeEtSCl)_2,PtCl_4$, melts at 211—212° and forms monoclinic crystals,

$$a : b : c = 1{\cdot}15113 : 1 : 0{\cdot}794745 ;\ \beta = 49^\circ\ 17'\ 56''.$$

Forms observed, (110), ($\bar{1}$11), (001), (010); combinations, (110) ($\bar{1}$11) (001) and (110)($\bar{1}$11) (001)(010).

Diethylmethylsulphine platinochloride, $(Et_2MeSCl)_2,PtCl_4$, melts at 205°, and crystallises in the monometric or cubic system; combinations, (100)(111). These crystals, when superficially observed, may easily be taken for monoclinic, owing to the development of one face, but their optical properties prove that they belong to the monometric system, as when examined by polarised light there are no signs of double refraction. This leaves unsettled the question as to whether sulphur is tetravalent or not. C. E. G.

Trimethylethyleneglycol from Methyl Isopropenyl Carbinol. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 32—34).—In a former paper, the author has shown that methyl isopropenyl carbinol when heated with dilute sulphuric acid (1 per cent. H_2SO_4), becomes converted into trimethylethylene glycol, whilst hydrochloric acid is without action at the ordinary temperature, but gives rise to products of condensation at a higher temperature. The author now finds that chlorine-derivatives of trimethylethylene yield trimethylethylene glycol, if left in contact with water in a closed flask at the ordinary temperature for several months. B. B.

Combination of Benzaldehyde with Polyhydric Alcohols. By MAQUENNE (*Compt. rend.*, **107**, 658—659).—The dibenzoic acetal of perseitol (perseite) previously described (this vol., p. 32), was made with alcohol of 85° to 90°, without addition of zinc chloride. It is assumed to be an acetal, because it resembles the product obtained by Meunier by the action of benzaldehyde on mannitol, and Friedel has pointed out that in all probability this is an acetal.

When a polyhydric alcohol containing an odd number of hydroxyl-groups is converted into an acetal, one of the hydroxyl-groups is left unattacked, and since the difference in composition between the acetals of two successive homologues can be detected by analysis, the conversion into acetals affords a convenient method of determining the number of hydroxyl-groups in a polyhydric alcohol.

C. H. B.

Constitution of Sorbinose. By H. KILIANI and C. SCHEIBLER (*Ber.*, **21**, 3276—3281).—Sorbinose behaves towards bromine and water similarly to levulose, and remains practically unchanged after a week; it contains therefore no aldehyde-group. When heated with nitric acid (sp. gr. = 1·39, 2 parts) for 40 hours at 35°, trihydroxyglutaric acid, $COOH\cdot[CH(OH)]_3\cdot COOH$ (this vol., p. 32), is formed. Potassium trihydroxyglutarate crystallises in monoclinic plates; $a : b : c = 1\cdot4641 : 1 : 0\cdot7094$; $\beta = 101° 3'$.

When sorbinose is reduced with hydriodic acid and amorphous phosphorus, it is converted, almost quantitatively, into hexyl iodide. Sorbinose has probably the constitution

$$OH\cdot CH_2\cdot[CH(OH)]_3\cdot CO\cdot CH_2\cdot OH.$$

N. H. M.

Changes suffered by Starch when Dissolved in Hot Glycerol. By K. ZULKOWSKI (*Chem. Centr.*, 1888, 1060, from *Ber. Oesterr. Gess. Chem. Ind.*, **10**, 2—4).—Starch, when heated in glycerol at 200°, produces a solution which gives a blue coloration with iodine at first, but which gradually changes to red. Addition of alcohol at this point precipitates erythrodextrin. If the heating is continued up to 210°, until the red coloration gives place to a brown one, alcohol precipitates achroodextrin. Other compounds are formed besides the two above named, and were separated by precipitation with barium hydroxide, &c., but were not further characterised.

J. W. L.

Derivatives of Allylamine. By C. PAAL (*Ber.*, **21**, 3190—3196; compare Gabriel, Abstr., 1888, 1267).—*Bromallylamine*, $C_3H_4Br\cdot NH_2$, is prepared by adding dibromopropylamine hydrochloride to excess of alcoholic potash, diluting the product with water, and distilling with steam. It is a colourless, mobile, very unstable oil, boils at 125° with partial decomposition, and mixes in all proportions with all ordinary solvents. When mixed with potassium carbonate, it is decomposed with separation of potassium bromide. When boiled for a long time with alcoholic potash, it seems to be, for the greater part, transformed into a hydroxy-base, but when the temperature is raised to 120—130°, it is completely decomposed. A crystalline salt, probably

$$C_3H_4Br{\cdot}NH{\cdot}C_3H_4{\cdot}NH_2,HBr,$$

is formed when bromallylamine is kept for a long time; the same salt remains when bromallylamine is distilled. Silver nitrate produces a white amorphous, and mercuric chloride a white crystalline precipitate in an aqueous solution of free bromallylamine. The *hydrochloride*, $C_3H_4Br{\cdot}NH_2,HCl$, crystallises in large needles or prisms, melts at 177—180°, and is readily soluble in water or hot alcohol. The *platinochloride*, $(C_3H_4Br{\cdot}NH_2)_2,H_2PtCl_6$, crystallises in yellow plates, and is readily soluble in hot water, but almost insoluble in absolute alcohol. The *aurochloride*, $C_3H_4Br{\cdot}NH_2,HAuCl_4$, crystallises in small, yellow needles, and decomposes when kept for some time in aqueous solution. The *hydrobromide*, $C_3H_4Br{\cdot}NH_2,HBr$, crystallises in large, colourless, quadratic prisms, melts at 223—224°, and is more sparingly soluble in alcohol and water than the hydrochloride. The *oxalate*, $C_3H_4Br{\cdot}NH_2,C_2H_2O_4$, crystallises in colourless plates, melts at 136—138°, and is readily soluble in water, but insoluble in alcohol and ether.

Tribromopropylamine hydrochloride, $C_3H_4Br_3NH_2,HCl$, prepared by adding bromine (1 mol.) to a well-cooled, concentrated aqueous solution of bromallylamine hydrochloride, crystallises from absolute alcohol in colourless needles. The free *base* is a heavy, yellow, very unstable oil with a pungent smell.

The *aurochloride*, $C_3H_4Br_3{\cdot}NH_2,HAuCl_4$, crystallises from water, in which it is moderately soluble, in golden-yellow plates, melting at 170°. The *platinochloride*, $(C_3H_4Br_3{\cdot}NH_2)_2,H_2PtCl_6$, crystallises from hot water in orange plates, and is decomposed when heated at 245°.

Isobutyldibromopropylamine hydrobromide, $C_4H_9{\cdot}NH{\cdot}C_3H_5Br_2HBr$, prepared by adding bromine (1 mol.) to a well-cooled glacial acetic acid solution of isobutylallylamine, crystallises from hot water, in which it is readily soluble, in slender needles, and is sparingly soluble in alcohol. The free *base* is a heavy, almost colourless, very unstable oil, with a feeble basic smell. When auric chloride is added to an aqueous solution of the hydrobromide, the *aurochloride* separates as a yellow oil, and then solidifies.

Butyldibromopropylamine hydrobromide, $C_4H_9{\cdot}NH{\cdot}C_3H_5Br_2,HBr$, can be prepared by treating butylbromallylamine with excess of dilute hydrobromic acid. It crystallises in large, concentrically grouped needles, and is readily soluble in water and hot alcohol. The *aurochloride* separates from an aqueous solution of the hydrobromide in flat needles, when auric chloride is added to an aqueous solution of the hydrobromide.

Butylbromallylamine, $C_4H_9NH{\cdot}C_3H_4Br$, can be prepared by boiling the isobutyldibromo-derivative with dilute alcohol for a long time, adding alkali, and distilling with steam. It can also be obtained by mixing the hydrobromide with excess of alcoholic potash in the cold, keeping the mixture for some time, diluting with water, and adding potassium carbonate, until the alcoholic solution of the base separates at the surface of the aqueous solution; the solution of the base is dried over potassium carbonate, poured into an alcoholic solution of oxalic acid, and the precipitated salt decomposed with alkali. It is a yellowish oil, with a camphor-like odour; it cannot be obtained in the pure state, as it is partially decomposed when distilled. The *oxalate*, $C_7H_{14}BrN,C_2H_2O_4$, crystallises in colourless needles, melts at 230—231°, and is moderately soluble in water.

Isoamyldibromopropylamine hydrobromide, $C_5H_{11}{\cdot}NH{\cdot}C_3H_5Br_2,HBr$, prepared by treating isoamylallylamine with bromine in glacial acetic acid solution, and then adding concentrated hydrobromic acid, crystallises in plates, melts at 230—231°, and is sparingly soluble in alcohol and cold water. The free *base* resembles the corresponding butyl base. The *platinochloride* is a reddish-yellow oil.

Amyldibromopropylamine hydrobromide, prepared by treating amylallylamine as described above, crystallises in needles, melts at 150°, and is moderately soluble in cold water and alcohol.

Isoamylbromallylamine, $C_5H_{11}{\cdot}NH{\cdot}C_3H_4Br$, prepared by treating isoamyldibromopropylamine hydrobromide with alcoholic potash, or by boiling the free base with dilute alcohol, is an oil; it is insoluble in water, and boils at about 150° with partial decomposition.

F. S. K.

Synthesis of Hydroxypropylenediisoamylamine. By E. Louïse (*Ann. Chim. Phys.*, **13**, 433—442).—*Hydroxypropylenediisoamylamine*, $C_{13}H_{29}NO$, is best prepared by heating propylenechlorhydrin (1 mol.) and diisoamylamine (at least 1½ mols.) at 100° in a closed vessel for 30 hours. The product is mixed with concentrated potash to decompose the diisoamylamine hydrochloride which is formed in the reaction, the mixture is again heated for 10 hours, and the oil which separates is dried over potassium carbonate and fractionated. The yield is 70 per cent. of the theoretical quantity, but it is impossible to get rid of the whole of the diisoamylamine by fractional distillation. The hydroxypropylene-derivative is obtained in the pure state by agitating the fractionated liquid with a small quantity of dilute, warm, hydrochloric acid, and decanting the supernatant oil. It is a colourless oil, with a somewhat disagreeable smell, and boils at 242—244°. It is sparingly soluble in water, but readily in alcohol, ether, and other solvents of the fatty series. All the simple salts, with the exception of the *picrate*, which is sparingly soluble, are syrupy liquids, and very readily soluble in water. The *platinochloride*, $(C_{13}H_{29}NO)_2,H_2PtCl_6$, separates from acidified alcohol in orange crystals, but the *aurochloride* is a yellow, sparingly soluble oil.

Propylenediisoamylamine benzoate, $C_{13}H_{28}N{\cdot}OBz$, is prepared by gradually adding a slight excess of benzoic chloride to a well-cooled, dry, ethereal solution of the alcohol, and, after evaporating the ether, heating the mixture at 100° for six hours in a sealed tube. The product is treated with boiling water, the cold mixture shaken with ether to remove benzoic acid, and the salt separated by adding potassium carbonate. It is a colourless oil, readily soluble in alcohol, ether, chloroform, &c., but insoluble in water. It is hydrolysed when boiled with potash, or when treated with strong acids, and is decomposed when distilled. This salt still has basic properties; its *oxalate*,

$C_{20}H_{33}NO_2,C_2H_2O_4$, crystallises from hot water or alcohol in slender, colourless needles, and is readily soluble in acetone and chloroform, but insoluble in ether. Most of its other salts do not crystallise and are very readily soluble, excepting the *platinochloride* and the *aurochloride*, which are only sparingly soluble.

Propylenediisoamylamine acetate, prepared in like manner, is a colourless oil, readily soluble in alcohol, ether, &c., but only sparingly in water. Its *oxalate* crystallises in needles, and is very readily soluble in alcohol and chloroform, but only moderately in water, and sparingly in ether. Its other salts are very readily soluble in water, and do not crystallise.
F. S. K.

Glyoxalbutyline and Glyoxalisobutyline. By J. Rieger (*Monatsh.*, 9, 603—612; compare Radziszewski, Abstr., 1883, 308, 728, 1086; 1884, 986).—*Glyoxalbutyline*, prepared according to the directions given by Radziszewski from glyoxal, ammonia, and normal butaldehyde, is a viscid, hygroscopic oil, having a sp. gr. of 1·0125 at 20°, and boiling under a pressure of 738 mm. at 266—268°. It is fairly soluble in water, and when an aqueous solution is treated with oxalic acid, the compound $(C_6H_{10}N_2)_2,C_2H_2O_4 + 2H_2O$ is formed; this crystallises in rhombic plates or long needles, and melts at 159—161°. The anhydrous oxalate, $(C_6H_{10}N_2)_2,C_2H_2O_4$, is precipitated as an amorphous, white powder on mixing alcoholic solutions of the acid and base. It partly sublimes at 170°, and melts with decomposition at 190—195°. The platinochloride, $2C_6H_{10}N_2,H_2PtCl_6$, crystallises in orange-red prisms, and on treatment with iodoparaffins gives the following bases:—

Oxalmethylbutyline, $C_6H_9MeN_2$, is a colourless, viscid liquid, having a sp. gr. of 0·9850 at 19·8°, and boils at 214—216° under a pressure of 722 mm. It dissolves readily in cold water, alcohol, ether, and chloroform. The platinochloride, $2C_6H_9MeN_2,H_2PtCl_6$, crystallises in orange-red, rhombic prisms.

Oxalethylbutyline, $C_6H_9EtN_2$, has a sp. gr. of 0·9593 at 16·5°, and boils at 218—222° under a pressure of 736 mm. The platinochloride is a yellow, amorphous powder.

Oxalpropylbutyline, $C_6H_9PrN_2$, is a liquid of sp. gr. 0·9393 at 18·9°. It boils at 226—228° under a pressure of 726 mm., and forms a platinochloride, insoluble in alcohol and ether, but readily soluble in hot water.

Oxalbutylbutyline, $C_4H_9{\cdot}C_6H_9N_2$, has a sp. gr. of 0·9379 at 18·9°, and boils at 242—245° under a pressure of 728 mm. It forms double salts with the chlorides of zinc, cadmium, and platinum, and on oxidation with hydrogen peroxide gives *butyloxamide*, $C_2H_3O_2N_2{\cdot}C_4H_9$, crystallising in lustrous needles, which sublime at 130°, and melt at 197—198°.

Oxalisobutylbutyline has a sp. gr. of 0·9403 at 13·4°, and boils at 231—233° under a pressure of 736 mm. The platinochloride forms orange-yellow needles, soluble in alcohol.

Oxalisoamylbutyline, $C_5H_{11}{\cdot}C_6H_9N_2$, has a sp. gr. of 0·9197 at 18·9°, and boils at 250—252° under a pressure of 724 mm. The platinochloride crystallises in rhombic needles.

Glyoxalisobutyline, prepared from isobutaldehyde, ammonia, and glyoxal, is a crystalline solid, melting at 125—126°, and boiling at 256—260°. It readily dissolves in hot water, alcohol, chloroform, and ether, and forms the salts $C_6H_{10}N_2,HCl$, melting at 105°, $C_6H_{10}N_2,HBr$, melting at 222°, and $C_6H_{10}N_2,C_2H_2O_4$, melting at 194—195°. By treatment with iodoparaffins, it furnishes the following bases:—

Oxalmethylisobutyline, C_6H_9MeN; this is a colourless, viscid oil, of sp. gr. 0·9576 at 16·6°, and boils at 205—206°. The platinochloride crystallises from water in orange-red plates, the compound $C_6H_9MeN_2,MeI$ in colourless, rhombic prisms, melting at 245—246°.

Oxalpropylisobutyline, $C_6H_9PrN_2$, which has a sp. gr. of 0·9299, and boils at 225—227°. The platinochloride crystallises in orange-red needles.

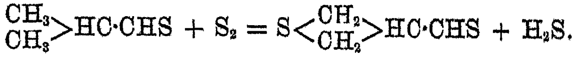
Oxalisoamylisobutyline; this has a sp. gr. of 0·9281 at 17·3°, and boils at 246—248° under a pressure of 738 mm. The platinochloride is scarcely soluble in alcohol, but dissolves readily in water.

All the oxalines described above turn yellow on exposure to the air, are miscible with alcohol, ether, and chloroform, and have characteristic unpleasant odours. G. T. M.

Action of Sulphur on Paraisobutaldehyde. By G. A. Barbaglia (*Gazzetta*, **18**, 85—88).—Unlike isobutaldehyde, sulphur has no action on the paraldehyde at 150°, but when heated with it for a long time (100 hours or more) at 180°, it becomes reddish-brown, and on opening the tube abundance of gas escapes, containing much hydrogen sulphide. The liquid has an acid reaction, and if left for a time separates into two layers. On submitting it to distillation, a liquid is obtained, which by means of fractional distillation can be separated into three portions; the first, distilling between 70° and 90°, was found on analysis to be isothiobutaldehyde; the second, distilling between 90° and 140°, has not yet been examined; whilst the third, 140—160°, is isobutyric acid. The reaction is probably in the first place—

$$4CHMe_2{\cdot}COH + S_2 = 2CHMe_2{\cdot}CSH + 2CHMe_2{\cdot}COOH,$$

but at the high temperature necessary for the reaction the excess of sulphur acts on the isothiobutaldehyde, converting it into polysulphide, with evolution of hydrogen sulphide—



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}HC{\cdot}CHS + S_2 = S{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}HC{\cdot}CHS + H_2S.$$

In all probability this product exists in the intermediate portion of the distillate. C. E. G.

Action of Ammonia on Methylethylacraldehyde. By E. Hoppe (*Monatsh.*, **9**, 634—657; compare Waage, Abstr., 1884, 172).—On passing ammonia into an ethereal solution of methylethylacraldehyde at 0°, a substance separates in white flakes, but is of so unstable a nature that it is impossible to isolate it. When heated in sealed tubes at 100° with excess of alcoholic ammonia, methylethylacraldehyde yields a viscid liquid which has a bitter taste and an odour resembling parvoline. No definite compound can be isolated from it, but its solution in hydrochloric acid gives white or yellow precipitates with most of the salts of the heavy metals. When heated in sealed tubes at 200° for 12 hours, the substance decomposes, and on opening the tube much ammonia is evolved. After several heatings in sealed tubes, no more ammonia is produced, and the following bases can be isolated from the residue:—(1) Picoline; (2) parvoline identical with that obtained by Waage, and yielding on oxidation α-β-pyridinedicarboxylic acid; (3) a new base, $C_{12}H_{19}N$, which forms a clear, mobile liquid having a pale blue fluorescence, a bitter taste, and a smell resembling parvoline but less intense. It dissolves readily in alcohol and ether, but is only slightly soluble in water. The platinochloride crystallises in orange-red, monoclinic prisms, is very soluble in alcohol, but only slightly so in water. G. T. M.

Action of Sulphurous Acid on Methylethylacraldehyde. By E. Ludwig (*Monatsh.*, 9, 658—674).—The author has further investigated the compound obtained by Lieben and Zeisel from sodium hydrogen sulphite and methylethylacraldehyde (Abstr., 1883, 570), and finds that it is most conveniently prepared by the direct addition of sulphurous acid to the unsaturated aldehyde. 10 grams of the aldehyde and 30 c.c. of water were introduced into a tube, and saturated with sulphurous acid at 0°; after sealing, the tube was heated at 80° for four hours, and the contents then neutralised with barium carbonate. The filtered solution, on concentration in a vacuum at 30°, gave barium hydroxyhexanedisulphonate, $C_6H_{12}O{:}(SO_3)_2Ba + 2H_2O$. The salt dissolves readily in water, is only slightly soluble in alcohol, and is very unstable. On heating with baryta-water, methylethylacraldehyde and barium sulphite are formed. If the contents of the tube, after heating, are diluted with an equal volume of water, and three-quarters of the liquid distilled off, the residue on neutralisation with barium carbonate and concentration in a vacuum over sulphuric acid gives the barium salt of capraldehydesulphonic acid, $(C_6H_{11}O{\cdot}SO_3)_2Ba$, as an amorphous mass. Capraldehydesulphonic acid can also be prepared by allowing aqueous sulphurous acid to react with methylethylacraldehyde at ordinary temperatures for several days, when all the oil disappears. From the solution, after saturation with barium carbonate and oxidation with bromine-water, barium sulphocaproate, $C_6H_{10}SO_5Ba$, crystallising in hexagonal plates may be isolated. *Sulphocaproic acid* may also be prepared from barium hydroxyhexanedisulphonate. The silver salt, $C_6H_{10}SO_5Ag_2$, crystallises in small plates, the calcium salt, $C_6H_{10}SO_5Ca + 1\frac{1}{2}H_2O$, in scales. On reduction with sodium amalgam in solutions containing free sulphuric acid, both hydroxyhexanedisulphonic acid and capraldehydesulphonic acid yield a sulphonic acid of hexyl alcohol, the sodium salt of which, $C_6H_{13}SO_4Na$, obtained in a slightly impure condition, forms an amorphous hygroscopic mass, and yields on distillation with lime a mixture of hexyl and hexenyl alcohols boiling at 149·6—151·6°. G. T. M.

Action of Potassium Cyanide on Ethyl α-Bromopropionate. Preparation of the Isomeric Symmetrical Dimethylsuccinic Acids. By N. Zelinsky (*Ber.*, **21**, 3160—3172).—Ethyl α-cyanopropionate and ethyl dimethylsuccinate are obtained when ethyl α-bromopropionate (250 grams) is boiled for about six hours with finely divided potassium cyanide (96 grams) in alcoholic solution (130 grams), the whole being constantly shaken. The yield is greater when the mixture is heated by a stream of hot air. The product is washed with water, dried, and fractionated. A small quantity of a crystalline substance is also formed in this reaction.

Ethyl α-cyanopropionate, CN·CHMe·COOEt, is a colourless liquid, boils at 197—198°, is not miscible with water, and yields a very hygroscopic sodium-derivative.

Ethyl dimethylsuccinate (compare Scherks, Abstr., 1882, 38) can be prepared by gradually adding ethyl α-bromopropionate (56 grams) to a mixture of sodium (0·72 gram) and ethyl α-cyanopropionate (4 grams) in alcoholic solution. It boils at 272—273° (compare Scherks, *loc. cit.*), and yields dimethylsuccinic acid melting at 192°, and the isomeric acid melting at 123—124°, when heated for 6—8 hours with hydrochloric acid (compare Otto and Beckurts, Abstr., 1885, 753; Otto and Rössing, Abstr., 1888, 45; also Bischoff and Hjelt, Abstr., 1888, 1057). Both acids yield the same anhydride when distilled. The anhydride crystallises in small plates melting at 87°. When the anhydride is boiled for a short time with a small quantity of water, it is almost entirely converted into the acid of lower melting point, but a small quantity of the isomeric acid is also formed.

F. S. K.

Solubility of the Silver, Calcium, and Barium Salts of Normal Caproic and Diethylacetic Acids. By P. Keppich (*Monatsh.*, **9**, 589—602; compare *ibid.*, **6**, 565).—The solubilities of the different salts were determined by Raupenstrauch's method. The formulæ deduced from these determinations are as follows:—

Silver normal caproate.... $S = 0{\cdot}07768 + 0{\cdot}0008268t + 0{\cdot}000031213t^2$.

Calcium normal caproate.. $S = 2{\cdot}727 - 0{\cdot}01475(t - 0{\cdot}7) + 0{\cdot}0002203\,(t - 0{\cdot}7)^2$.

Barium normal caproate .. $S = 9{\cdot}47 - 0{\cdot}08975\,(t - 0{\cdot}5) + 0{\cdot}0014983\,(t - 0{\cdot}5)^2$

Silver diethylacetate ..... $S = 0{\cdot}402 + 0{\cdot}000847\,(t - 0{\cdot}7) + 0{\cdot}000038\,(t - 0{\cdot}7)^2$

Calcium diethylacetate ... $S = 30{\cdot}119 - 0{\cdot}2617\,(t - 0{\cdot}7) + 0{\cdot}001498\,(t - 0{\cdot}7)^2$.

Barium diethylacetate is so intensely soluble in water, that the author did not succeed in obtaining any analytical results.

G. T. M.

Chlorine-derivatives of Ethyl Acetoacetate. By P. Genvresse (*Compt. rend.*, **107**, 687—689).—When chlorine is passed into ethyl acetoacetate, the temperature rises to 165° but afterwards falls, and the chief products are the di- and tri-chlorinated derivatives, together with small quantities of higher substitution products.

When the dichloro-derivative is heated in sealed tubes with dilute hydrochloric acid, it yields unsymmetrical dichloracetone, water, and alcohol, and hence it has the constitution $CHCl_2 \cdot CO \cdot CH_2 \cdot COOEt$. When treated with chlorine at 170°, it yields the tri-derivative, together with small quantities of the tetra- and penta-derivatives.

The trichloro-derivative, when heated with dilute hydrochloric acid in sealed tubes at 170°, yields trichloracetone, $CCl_3 \cdot COMe$, alcohol, and carbonic anhydride, so that its constitution is $CCl_3 \cdot CO \cdot CH_2 \cdot COOEt$, and not $CHCl_2 \cdot C(OH){:}CCl \cdot COOEt$, as supposed by Mewes.

Ethyl tetrachloracetoacetate boils with partial decomposition at 229—231° under ordinary pressure, and with less decomposition at 153—157° under a pressure of 40 mm. It is colourless, and heavier than water; when heated with dilute hydrochloric acid under pressure, it yields carbonic anhydride, alcohol, and unsymmetrical tetrachloracetone, so that its constitution is $CCl_3 \cdot CO \cdot CHCl \cdot COOEt$.

Ethyl pentachloracetoacetate boils at 240—244° under ordinary pressure, or at 164—168° under a pressure of 35 mm., and is a colourless liquid heavier than water. When heated at 160° with dilute hydrochloric acid, it yields carbonic anhydride, alcohol, and pentachloracetone, so that its constitution is $CCl_3 \cdot CO \cdot CCl_2 \cdot COOEt$.

If ethyl acetoacetate is subjected to the action of chlorine at 150° to 220° for 10 days, derivatives containing 7 and 9 atoms of chlorine are obtained. The former, $CCl_3 \cdot CO \cdot CCl_2 \cdot COOC_2H_3Cl_2$, is a syrupy almost colourless liquid which boils at 270—272° with much decomposition under ordinary pressure, or with slight decomposition at 220—225° under a pressure of 110 mm. The derivative with 9 atoms of chlorine, $CCl_3 \cdot CO \cdot CCl_2 \cdot COOC_2HCl_4$, is a syrupy liquid which does not solidify at —23°, and boils at 225—230° under a pressure of 40 mm.

Methyl acetoacetate yields similar derivatives. C. H. B.

Dihydroxystearic Acid obtained by the Oxidation of Oleic Acid with Potassium Permanganate in Alkaline Solution.

By N. SPIRIDONOFF (*J. Russ. Chem. Soc.*, 1887, **19**, 646—654).—The dihydroxystearic acid was prepared by Syrneff and Saytzeff's method from ordinary oleic acid, and the present paper contains a determination of its constants. Solubility in ethyl alcohol of 99·5 per cent. at 19°, 100 pts. of solution contain 0·59 pt. of the acid, dry ethyl ether at 18° = 0·19 pt. The ethyl salt (m. p. 93·8—100°) was obtained by the action of hydrogen chloride on an alcoholic solution of the acid. Solubility in alcohol of 91·5 per cent., 100 pts. of the solution at 16° contain 4·58 pts.; at 18° = 4·72 pts.; ethyl ether at 18° = 1·75 pts. The methyl salt (m. p. 105—106·5°), 100 pts. of the alcoholic solution at 18·5° contain 3·34 pts.; dry ether at 19° = 1·03 pts. The acetyl-derivative was obtained by the action of acetic anhydride at 150° on the acid. It is a colourless, viscid liquid, and its composition is $C_{18}H_{34}Ac_2O_4$. Oxidation with potassium permanganate in alkaline solution yielded, as the chief products, caprylic, suberic, and azelaïc acids, together with some unchanged dihydroxystearic acid. This was proved by the analysis of the free acids and their salts. The same acids are found among the products of oxidation of oleic acid, and are therefore only products of the oxidation of dihydroxystearic acid. B. B.

Action of Allyl Iodide and Zinc on Ethyl Malonate. By V. Matvéeff (*J. Russ. Chem. Soc.*, 1887, **19**, 643—646).—Following the method by which Schukoffsky prepared the ethyl salt of diethylmalonic acid (Abstr., 1888, 1179), the author by the mutual action of allyl iodide, zinc, and ethyl malonate, has obtained *ethyl diallylmalonate*, $C(C_3H_5)_2(COOEt)_2$, together with free propylene. The ethyl salt is an oily liquid boiling at 239—241°, and having the sp. gr. 0·99181 at 20°, 0·98707 at 30°, and 3·98085 at 35°. The free acid obtained by hydrolysis of the ethyl salt, is described, and also the corresponding sodium, calcium, and silver salts. B. B.

Action of Maleïc Acid on Aniline. By I. Ossipoff (*J. Russ. Chem. Soc.*, 1888, **20**, 83—97).—Referring to the work done by Perkin, Michael, Wing, and Palmer, and especially by Anschütz and Wirtz, on the constitution of maleïc acid, the author tried to solve the problem in the following manner:—Hydrogen sodium maleate was dissolved in water and boiled with aniline in a flask furnished with a reflux condenser, when crystals were formed which were greenish-yellow, melted at 141—143°, and left no ash on incineration. They are only sparingly soluble in ether, chloroform, benzene, and light petroleum, but easily in alcohol. After purification they become white, and the melting point rises to 144—145°. Elementary analysis, however, proved that the substance is not homogeneous; the principal constituent is the aniline salt of phenylaspartic acid or its isomeride. The product was treated with baryta-water, and the barium, lead, and silver salts prepared. With acetic anhydride, it yields acetanilide. With diphenylamine, it gives a substance melting at 207—208°, probably phenylaspartanil. The liquid from which the crystals have separated contains a mixture of sodium salts. The author concludes that maleïnanil is the anil of maleïc acid, and phenylaspartanil the anil of a lactone isomeric with phenylaspartic acid. B. B.

Isomerism of Fumaric and Maleïc Acids. By I. Ossipoff (*J. Russ. Chem. Soc.*, 1888, **20**, 97—108).—A purely theoretical paper based on the results described above. B. B.

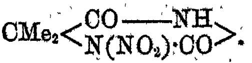
Methyl and Ethyl Salts of Ethylenediamidoformic Acid and their Nitro-derivatives. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, **7**, 258—262).—The methyl salt, $C_2H_4(NH{\cdot}COOMe)_2$, is easily obtained in almost theoretical quantity on mixing methyl carbonate (2 mols.) with ethylenediamine (1 mol.). It is very soluble in boiling water, alcohol, and chloroform, but less soluble in ether and benzene, and melts at 132—133°. It dissolves in concentrated nitric acid with development of heat, and on adding water to this solution a white powder is precipitated, having the melting point of the original compound, but containing 21·23 per cent. N, the original compound having only 16·41 per cent. It is nearly insoluble in cold, but more soluble in hot water, very soluble in chloroform and benzene, but only slightly in ether and alcohol. From all solvents it separates in slender needles.

The ethyl salt has already been described by Fischer and Koch under the name ethylenediurethane. The authors have obtained it along with various bye-products by heating a mixture of ethyl carbonate and ethylenediamine at about 200° for 16 hours, as a colourless substance soluble in ether. The nitro-derivative is obtained in like manner to that of the methyl salt. It is a compound of very similar properties, melting at 83—84°. Analysis shows that it is a dinitro-derivative. Distilled with aqueous potash, it gives a distillate, which on the addition of potassium carbonate separates into two layers. The upper contains ethyl alcohol, and the lower ethylene dinitramine. This nitro-derivative therefore has the constitution $C_2H_4[N(NO_2)\cdot COOEt]_2$. H. C.

Ureides and their Nitro-derivatives. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, **7**, 236—257).—The authors distinguish—(1.) Ureides of bibasic acids, in which each of the two NH-groups is between two CO-groups; these do not yield nitro-derivatives. (2.) Ureides of monobasic acids, in which one of the NH-groups is between two CO-groups, and the other between a CO-group and the hydrocarbon residue; these give mononitro-derivatives. (3.) Ureides in which each NH-group is attached to a hydrocarbon residue, and neither lies between two CO-groups. These last compounds yield dinitro-derivatives, and the name "*ureines*" is proposed for them. A number of the nitro-derivatives of (2) and (3) have been considered in a former paper (Abstr., 1888, 1180), and the present is a continuation of this work.

Nitrohydantoïn when boiled with 25 times its weight of water loses 1 mol. of carbonic anhydride, and takes up 1 mol. of water, being converted into nitramidoacetamide, which on further evaporation of the aqueous solution yields glycolamide. Nitro-lactylcarbamide treated in the same manner loses carbonic anhydride and nitrous oxide, and yields an acid solution, which gives with cobalt acetate the reaction for lactic acid.

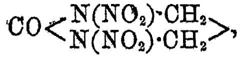
Nitroacetonylcarbamide is prepared by evaporating acetonylcarbamide with five times its weight of nitric acid, and recrystallising the residue from absolute alcohol or benzene. It forms slender, colourless needles, melting at 140—141°. Its probable constitution is



$$CMe_2<\begin{matrix}CO\text{——}NH\\N(NO_2)\cdot CO\end{matrix}>.$$

When boiled with 25 times its weight of water, it loses carbonic anhydride and nitrous oxide, and appears to yield α-hydroxybutyramide and α-hydroxybutyric acid.

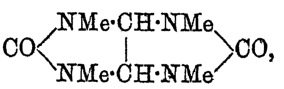
Ethylenedinitrureine (*ethylenedinitrocarbamide*),



$$CO<\begin{matrix}N(NO_2)\cdot CH_2\\N(NO_2)\cdot CH_2\end{matrix}>,$$

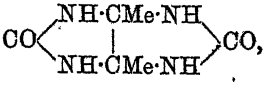
gives a compound with 4 mols. NaOH, soluble in water and insoluble in alcohol, and with 4 mols. $AgNO_3$ a white compound which detonates violently on heating. On boiling with water, it yields ethylenedinitramine; this compound forms salts containing 2 mols. of the metal. Heated with dilute sulphuric acid, it loses nitrous oxide, and gives aldehyde and glycol. Reduction experiments have up to the present led to no definite results.

Acetylenetetramethyldiureine (tetramethylglycolurile),

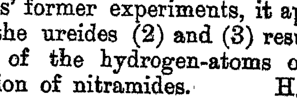


is prepared by evaporating on a water-bath aqueous solutions of glyoxal and dimethylcarbamide, to which a few drops of hydrochloric acid have been added. It crystallises in long, colourless, brittle needles, of bitter taste, melting at 217°, very soluble in water, alcohol, and chloroform, and slightly soluble in ether and benzene. On treatment with strong nitric acid, it is converted into *acetylenetrimethylmononitrodiureine* by the displacement of one of the methyl-groups by the nitro-group. The nitro-derivative crystallises in fine, colourless needles, melting at 225—226°, not very soluble in water or alcohol, and still less so in ether and benzene.

Dimethylacetylenediureine (dimethylglycolurile),



separates as a white powder when a mixture of 20 parts of diacetyl, 50 parts of water, and 35 parts of carbamide is left for 24 hours. It is slightly soluble in water, from which it crystallises in slender needles or small prisms; it is very slightly soluble in alcohol, and not at all in ether, chloroform, or benzene. With nitric acid, it yields a dinitro-derivative, which on boiling with water loses carbonic anhydride and nitrous oxide, and gives diacetyl and carbamide. This nitro-derivative probably has the constitution



From the above and the authors' former experiments, it appears that the action of nitric acid on the ureides (2) and (3) results in the displacement of one or more of the hydrogen-atoms of the NH-groups by NO_2, and the formation of nitramides. H. C.

Identity of Methronic Acid and Sylvanecarboxyacetic Acid. By R. Fittig and A. Hantzsch (*Ber.*, **21**, 3189—3190; compare Fittig and Schloesser, Abstr., 1888, 1089, Polonowsky, *ibid.*, 1175).—The acid obtained from glyoxal and ethyl acetoacetate (compare

Polonowsky, Abstr., 1888, 1067) is identical with methronic acid prepared from ethyl acetoacetate and sodium succinate. The same monobasic acid is obtained by the distillation of carbopyrotritaric acid, methronic acid, and sylvanecarboxyacetic acid. F. S. K.

Isomeric Changes on Synthesising Aromatic Compounds by means of Aluminium Chloride. By J. SCHRAMM (*Monatsh.*, 9, 613—625).—When isobutyl bromide (300 grams) is allowed to drop very slowly into a mixture of benzene (900 grams) and aluminium chloride (300 grams) kept cool with ice, a butylbenzene (yield 60 per cent.) having a sp. gr. of 0·8718 at 15°, and boiling at 167—167·5° under a pressure of 736 mm., is formed. It does not agree in its properties with the isobutylbenzene boiling at 170—170·5°, sp. gr. 0·8578 at 15°, formed by Fittig's method (Gossin, Abstr., 1884, 1312), for the product, on treatment with 1 mol. of bromine in presence of iodine, gives a monobromobutylbenzene boiling at 230—231·5° under a pressure of 736 mm., readily solidifying on cooling, and melting at 13—14°, whilst the monobromobutylbenzene from the butylbenzene prepared by Fittig's method, boils at 232—233·5°, and does not solidify at −20°. The product of the synthesis is therefore *trimethylphenylmethane* (*tertiary butylbenzene*), CMe_3Ph. Gossin's butylbenzene, boiling at 152—155°, was not formed.

Tertiary butyl chloride (50 grams), benzene (150 grams), and aluminium chloride (50 grams) under similar conditions give tertiary butylbenzene (yield 60 per cent.). In this case no isomeric change takes place, but normal butyl chloride (75 grams), benzene (300 grams), and aluminium chloride (80 grams) give secondary butylbenzene, CHMeEtPh, boiling at 173·5—174·5°, under a pressure of 735 mm.), and having a sp. gr. of 0·8669 at 15°; it is identical with the butylbenzene which Radziszewski prepared from α-phenylethyl bromide and zinc ethyl. Isoamyl chloride (170 grams), benzene (360 grams), and aluminium chloride (170 grams) give an *amylbenzene* (20 per cent. yield) which boils at 187·5—188·5 under a pressure of 737 mm., and has a sp. gr. of 0·8683 at 15°. It therefore does not correspond with the isoamylbenzene which Essner (Abstr., 1882, 46) prepared from isoamyl bromide and bromobenzene, and must consequently be represented by one of the formulæ $CHMePh{\cdot}CHMe_2$ or CMe_2EtPh, isomeric change having taken place.

It follows from the above that when the primary monochloroderivatives of the fatty series act on benzene in presence of aluminium chloride, the phenyl-group does not take up the position of the halogen, but links itself to another carbon-atom, thereby forming a secondary or tertiary hydrocarbon. The isomeric change is not analogous to that of normal- into iso-propyl bromide in presence of aluminium chloride, as observed by Kekulé and Schrötter (*Ber.*, **12**, 2280), moreover Essner has shown that isoamyl chloride does not behave similarly. On the contrary, the author finds that isobutyl chloride in presence of aluminium chloride splits up into hydrogen chloride and butylene, and holds the opinion that the isomeric changes depend on a reaction similar to that observed by Bahlsohn (Abstr., 1879, 785), who found that ethylbenzene could be prepared from benzene and ethylene in presence of aluminium chloride. He therefore concludes that the chloroparaffin splits up into hydrogen chloride and the corresponding olefine, which reacts with the benzene in the following way:—$PhH + Me_2C{:}CH_2 = CPhMe_3$, the phenyl-group attaching itself to the carbon-atom, which is directly united to the smallest number of hydrogen-atoms. G. T. M.

Orthocresol. By A. Claus and U. A. Jackson (*J. pr. Chem.* [2], **38**, 321—336).—Wroblewsky is mistaken in regarding the golden-yellow needles obtained by the action of nitrous acid on bromorthotoluidine as bromocresol, for they are really nitrobromorthocresol. During the action, parabromorthocresol is formed as well as the nitro-compound; to separate them, the acid liquid is distilled with steam and the yellow oil thus obtained, which partially solidifies on cooling, treated with weak sodium carbonate solution; the red solution thus formed is shaken with ether, which dissolves the bromocresol; the alkaline solution is then precipitated with weak hydrochloric acid, and the precipitate sublimed, when *nitrobromorthocresol*, [$OH : Me : Br : NO_2 = 1 : 2 : 4 : 6$], is obtained, forming beautiful golden-yellow needles, melting at 88° (uncorr.), and having all the properties of Wroblewsky's bromorthocresol. The *sodium* salt crystallises in red prisms, having a green lustre.

Amidobromorthocresol, [$OH : Me : Br : NH_2 = 1 : 2 : 4 : 6$], is formed when the nitro-compound is reduced with stannous chloride and strong hydrochloric acid in alcoholic solution; it crystallises from ether as a white mass which rapidly becomes brown, and sublimes in colourless needles melting at 110° (uncorr.); its *hydrochloride* is described.

Parabromorthocresol, [$OH : Me : Br = 1 : 2 : 4$] may be prepared from bromorthotoluidine as above, or by dropping a chloroform solution of bromine into a similar solution of orthocresol containing one-tenth of its weight of iron wire. It crystallises from hot water and from alcohol in colourless needles which sublime unchanged; it melts at 64° (uncorr.), and boils at 235° (uncorr.). When orthoparadibromocresol (Werner, Abstr., 1886, 1015) is oxidised by chromic acid in an acetic acid solution, *metabromotoluquinone*, [$Me : Br : O : O = 1 : 3 : 2 : 5$], is precipitated in yellow flocks, which crystallises from ether in yellow prisms, subliming as needles, which melt at 93° (uncorr.), and are sparingly soluble in water, freely so in other solvents; when an ethereal solution of it is shaken with a hydrochloric acid solution of stannous chloride until it is decolorised, the corresponding *quinol* is obtained; this forms white laminæ which melt at 112° (uncorr.) and dissolve easily in the usual solvents; the *acetyl*-derivative melts at 57° (uncorr.). By chlorinating a glacial acetic acid solution of parabromorthocresol, *chlorobromorthocresol*, [$OH : Me : Br : Cl = 1 : 2 : 4 : 6$], is obtained; it crystallises in colourless needles melting at 48° (uncorr.), and yields chlorotoluquinone on oxidation (comp. Abstr., 1886, 614). *Parachlororthocresol*, [$OH : Me : Cl = 1 : 2 : 4$], is obtained by chlorinating a glacial acetic acid solution of orthocresol containing some iron; the oil crystallises with difficulty, and by sublimation yields crystals melting at 33° (uncorr.), and boiling at 220° (uncorr.).

The authors describe orthocresolparasulphonic acid and its *potassium* (2 mols. H_2O) and *barium* salts; orthocresolorthosulphonic acid and its *potassium* salt (1 mol. H_2O); orthocresolorthoparadisulphonic acid and its *potassium* (2 mols. H_2O), *barium*, *copper*, and *lead* salts; but these acids have been described before. *Bromocresolparasulphonic acid*, $[OH : Me : Br : SO_3H = 1 : 2 : 4 : 6]$, is obtained as its *potassium* salt (1 mol. H_2O) by brominating potassium orthocresolparasulphonate, and as its *barium* salt by treating this with barium chloride; the free acid melts in its water of crystallisation at 95° (uncorr.).; the *calcium* (3 mols. H_2O), *copper*, *lead* (3 mols. H_2O) and *silver* salts are described. The parabromorthocresolorthosulphonic acid is obtained from orthocresolorthosulphonic acid in a similar way. A. G. B.

Dinitrortho-xylenols. By E. Nölting and B. Pick (*Ber.*, **21**, 3158—3160).—Dinitrortho-xylenol, $[OH : Me_2 : (NO_2)_2 = 1 : 3 : 4 : 2 : 6]$, is obtained when the yellow ammonium salt formed in the preparation of nitro-xylene (compare Jacobsen, Abstr., 1884, 737) is decomposed with acids; it can also be prepared by nitrating 1 . 2 . 4-ortho-xylidine and diazotising the product. It crystallises in yellow needles, melts at 127°, and is readily soluble in boiling alcohol, but only sparingly in water and cold alcohol. The ammonium salt is sparingly soluble in cold, but more readily in hot water. The isomeric compound, $[OH : Me_2 : (NO_2)_2 = 1 : 2 : 3 : 4 : 6]$, is obtained in like manner from 1 . 2 . 3-ortho-xylidine. It crystallises from alcohol in small, yellow needles, melts at 82°, and forms an *ammonium* salt which crystallises in needles and is moderately soluble in water. Concentrated aqueous solutions of the ammonium salts described above give orange or yellow crystalline precipitates with barium or calcium chloride and other inorganic salts. F. S. K.

Benzene-derivatives of High Molecular Weight. By F. Krafft and J. Göttig (*Ber.*, **21**, 3180—3188; compare Krafft, Abstr., 1887, 252; 1888, 1087).—*Hexadecylphenetoïl*, $C_{16}H_{33}{\cdot}C_6H_4{\cdot}OEt$, is prepared by heating hexadecylphenol with ethyl iodide and alcoholic potash. It crystallises from alcohol in plates and melts at 43—44°. It yields parethoxybenzoic acid, melting at 195°, when heated at about 120° with nitric acid of sp. gr. 1·12.

Acethexadecylanilide, $C_{16}H_{33}{\cdot}C_6H_4{\cdot}NHAc$, prepared by treating amidohexadecylbenzene with acetic chloride, melts at 104—104·5°, and boils at about 295° (15 mm.).

Orthomethylhexadecylbenzene, $C_{16}H_{33}{\cdot}C_6H_4Me$, is obtained by heating a mixture of sodium (10 grams), orthobromotoluene (34 grams), and cetyl iodide (48 grams) at about 140°. It crystallises from a well-cooled mixture of ether and alcohol, melts at 8—9°, and boils at 238·5—239° (15 mm.). It resembles hexadecylbenzene in its behaviour towards solvents, and the melted substance is fluorescent. The corresponding *meta*-derivative, prepared in like manner, melts at 11—12°, boils at 236·5—237° (15 mm.), and resembles hexadecylbenzene in its behaviour towards solvents. The *para*-derivative melts at 27·5° and boils at 239·5—240° (15 mm.). The melted substance solidifies to a mass of crystals, but does not melt again at 27·5° until it has been either well cooled or brought into contact with a crystal of the original substance. It yields toluylic acid when heated at 120—130° with nitric acid of sp. gr. 1·12.

Sodium paramethylhexadecylbenzenesulphonate, $C_{16}H_{33}\cdot C_6H_3Me\cdot SO_3Na$, is obtained in nacreous plates when the preceding compound is dissolved in fuming sulphuric acid, the product poured into ice-cold water, the acid extracted with ether and treated with sodium chloride.

Paramethylhexadecylphenol, $C_{16}H_{33}.C_6H_3Me\cdot OH$, prepared by melting the preceding compound with potash and a little water at 150°, crystallises from alcohol, melts at 62°, and boils at 267—268° (15 mm.).

Paramethylhexadecylphenetoïl, obtained by heating the phenol with ethyl iodide and alcoholic potash, melts at 26·5.°

Amidoparamethylhexadecylbenzene, $C_{16}H_{33}\cdot C_6H_4Me\cdot NH_2$, is obtained when paramethylhexadecylbenzene is dropped into cool, fuming nitric acid, and the resulting nitro-compound, melting at about 40°, reduced with stannous chloride. It melts at about 54° and boils at 264—265° (15 mm.).

Dimethylhexadecylbenzene, $[Me_2 : C_{16}H_{33} = 1 : 3 : 4]$, prepared by heating bromometaxylene and cetyl iodide with sodium, crystallises from a well-cooled mixture of ether and alcohol, melts at 33·5° and boils at 249·5—250°.

Trimethylhexadecylbenzene, $[Me_3 : C_{16}H_{33} = 1 : 3 : 5 : 6]$, prepared in like manner from bromomesitylene, seems to melt at about 40° and boils at 258—258·5° (15 mm.). F. S. K.

Constitution of Styphnic Acid. By S. KOSTANECKI and B. FEINSTEIN (*Ber.*, 21, 3119—3123).—Consecutive dinitroresorcinol is best prepared by the method Stenhouse and Groves employed in the case of dinitroorcinol. (This Journal, 1877, i, 545.)

Styphnic acid is obtained by boiling consecutive dinitroresorcinol with dilute nitric acid and by the action of very strong nitric and sulphuric acids on the symmetrical dinitro-derivative in the cold. The acid has therefore the constitution $[(OH)_2 : (NO_2)_3 = 1 : 3 : 2 : 4 : 6]$, ascribed to it by Nölting and Collin (Abstr., 1883, 1004).

N. H. M.

Action of Carbon Bisulphide on Dimethylaniline in Presence of Nascent Hydrogen.—By J. WIERNIK (*Ber.*, 21, 3204—3207).—When dimethylaniline and carbon bisulphide are treated with zinc-dust and hydrochloric acid, tetramethyldiamidophenylmethane melting at 90° and thioformaldehyde are formed. The former compound is identical with that obtained by Tröger (Abstr., 1888, 287), who took it for the ethane-derivative. This, however, crystallises in slender needles and melts at 50° (Schoop, Abstr., 1881, 160). N. H. M.

1.2.3-Metaxylidine and its Identity with Wroblewsky's Orthoxylidine. By E. NÖLTING and B. PICK (*Ber.*, **21**, 3150—3154; compare Grevingk, Abstr., 1885, 144, and Nölting and Forel, Abstr., 1886, 58).—Metaxylidine can be obtained from commercial xylidine as follows:—The bases are converted into the sulphates, the solution is allowed to crystallise, and the mixture of bases obtained from the mother-liquor from the last crop of crystals is fractionated. The portion distilling at 212—216° is treated with acetic anhydride, and the mixture of acetyl-derivatives boiled for a few hours with four times its weight of 25 per cent. sulphuric acid. On cooling, the greater part of the metaceto-xylide separates unchanged, and the remainder can be obtained by extracting the diluted mother-liquor with ether. The acetyl-derivative is then decomposed by heating at 150° with concentrated hydrochloric acid or at 200° with three times its weight of 70—75 per cent. sulphuric acid. Metaxylidene can also be prepared from commercial xylidine by heating the mixture of bases obtained from the mother-liquor from the sulphates (see above) for 24 hours with an equal weight of glacial acetic acid and distilling the product. The portion passing below 300° is then treated with acetic anhydride and the acetyl-derivative boiled with 25 per cent. sulphuric acid and isolated as described above. The fraction passing above 300° contains a small quantity of metaceto-xylide, which can be separated by heating with 25 per cent. sulphuric acid as already described. The *sulphate*, $(C_8H_9NH_2)_2,H_2SO_4$, crystallises in needles, and is decomposed into *hydrogen xylidine sulphate*, $C_8H_9NH_2,H_2SO_4 + 2\frac{1}{2}H_2O$, when the aqueous solution is evaporated.

1.2.3-Metaxylidine is only with difficulty converted into the acetyl-derivative; the latter melts at a comparatively high temperature, and is hydrolysed only with difficulty. The sulphate is very readily soluble. In these respects, this base differs from all the isomeric compounds.

The compounds described by Wroblewsky (*Ber.*, **18**, 2904, 3106; **19**, 235) as ortho-xylidine is identical with 1.2.3-metaxylidine.

F. S. K.

Metaxylylamidomethane. By W. HINRICHSEN (*Ber.*, **21**, 3082—3086).—Metaxylonitrile, prepared from metaxylidine by Sandmeyer's reaction, melts at 23—25°. *Metaxylylamidomethane* (*metaxylobenzylamine*), $C_6H_3Me_2\cdot CH_2\cdot NH_2$, prepared by treating a hot alcoholic solution of metaxylonitrile (10 grams) with sodium (16 grams), boils at 218—219°, is readily soluble in alcohol and ether, sparingly in water, and absorbs carbonic anhydride and water on exposure to the air. The *hydrochloride*, $C_9H_{13}N,HCl$, crystallises in needles or plates and melts at 210°. The *hydriodide* is crystalline. The *platinochloride*, $(C_9H_{13}N)_2,H_2PtCl_6$, crystallises in small, yellow needles, melting at 226—228° with decomposition. The *mercurochloride*, $C_9H_{13}N,HHgCl_3$, crystallises in large plates or needles, melts at 205°, and is very sparingly soluble in water. The *sulphate* crystallises from water in needles, melting at 254°. The *picrate*, $C_9H_{13}N,C_6H_3N_3O_7$, crystallises in yellow plates and melts at 223° with decomposition. The *nitrate* crystallises in slender needles melting at 157—158°. The salt, $C_9H_{13}N,CdI_2$, prepared by adding a solution of potassium cadmium iodide to a solution of the base, is crystalline and moderately soluble in water. The *cadmioiodide*, $(C_9H_{13}N)_2,2HI,CdI_2$, prepared by adding a solution of potassium cadmium iodide to an aqueous solution of the hydrochloride, is only moderately soluble in alcohol and very sparingly so in water.

Metaxylyl carbinol (metaxylobenzyl alcohol), $C_6H_3Me_2{\cdot}CH_2{\cdot}OH$, is prepared by treating the preceding compound with nitrous acid and distilling the product with steam. It is a colourless, aromatic-smelling liquid, boils at about 232°, solidifies when cooled in a freezing mixture and melts at 22°.

Dimethylbenzaldehyde (metaxylobenzaldehyde), $C_6H_3Me_2{\cdot}CHO$, is formed when the alcohol is oxidised with sulphuric acid and potassium dichromate. The product is distilled with steam and purified by means of the crystalline sodium hydrogen sulphite compound. It is a colourless oil, boils at 223—225°, smells like benzaldehyde, and turns yellowish on exposure to the air. F. S. K.

Action of Amines on Nitrogenous Organic Compounds.

By B. LACHOWICZ (*Monatsh.*, 9, 695—700).—When hydrobenzamide is gently warmed with the amines, decompositions occur which may be represented by the general equation $N_2(CHPh)_3 + 3RNH_2 = 2NH_3 + 3CHPh{:}NR$. By means of this reaction, the author has formed the following derivatives of benzylidene:—

$C_7H_6{:}NPh$, prepared from aniline, agrees with the description given of it by Cech (Abstr., 1878, 408), except that its melting point is 49°, whereas Cech gives it as 42°.

$C_7H_6{:}N{\cdot}C_6H_4Cl$, prepared from metachloraniline, is a viscid liquid which boils at 338°.

$C_7H_6{:}NC_6H_3Cl_2$, prepared from paradichloraniline (m. p. 63°), crystallises from alcohol in thin plates melting at 84°.

$C_7H_6{:}N{\cdot}C_6H_4{\cdot}NO_2$, prepared from paranitraniline, crystallises in yellow needles melting at 115°; the compound prepared from metanitraniline crystallises in yellow needles melting at 73°.

$C_7H_6{:}N{\cdot}C_7H_7$, prepared from orthotoluidine, forms an oil, boiling at 309—310° (745 mm.).

$C_7H_6{:}N{\cdot}C_{10}H_7$, prepared from α-naphthylamine, crystallises from alcohol in yellow needles melting at 73°. The compound from β-naphthylamine forms yellow needles melting at 101°.

$CHPh(C_5NH_{10})_2$, prepared from piperidine, melts at 81°.

The amides of the acids react with hydrobenzamide with evolution of ammonia, strong bases such as piperidine and formamide being similarly decomposed. G. T. M.

Condensation Products from Bases of the Para-series with Para- and Meta-nitrobenzaldehyde.

By A. BISCHLER (*Ber.*, 21, 3207—3219; compare Abstr., 1888, 287).—*Diacetyl-β-paranitrophenyl-diparamidotolylmethane*, $NO_2{\cdot}C_6H_4{\cdot}CH(C_7H_6{\cdot}NHAc)_2$, prepared by boiling the base with a slight excess of acetic anhydride for one or two hours, crystallises from dilute alcohol in light yellow grains melting at 136°. It is readily soluble in cold alcohol and ether. The *benzoyl-derivative*, $C_7H_5NO_2(C_7H_6{\cdot}NHBz)_2$, is obtained by heating the base with benzoic anhydride at 120—130°; it forms yellow needles, melts at 152°, and is readily soluble in warm alcohol and ether.

β-Metanitrophenyldiparamidotolylmethane,

$$NO_2{\cdot}C_6H_4{\cdot}CH(C_7H_6{\cdot}NH_2)_2,$$

is prepared by adding strong sulphuric acid to an intimate mixture of metanitrobenzaldehyde and paratoluidine sulphate; after three to four days it is treated with much water and heated; it is then filtered, made alkaline, and steam distilled. The oily residue, which solidifies when cold, is crystallised from hot alcohol. It crystallises in yellowish needles, melts at 85—86°, dissolves very readily in chloroform, readily in hot alcohol, rather readily in ether and benzene. The *hydrochloride* forms voluminous, yellowish needles, readily soluble in hot alcohol; hot water decomposes it. The *platinochloride*, $C_{21}H_{21}N_3O_2,H_2PtCl_6$, crystallises in yellow, voluminous needles, sparingly soluble in alcohol. The *acetyl-compound*, $NO_2{\cdot}C_6H_4{\cdot}CH(C_7H_6{\cdot}NHAc)_2$, separates from the aqueous alcoholic solution in pale yellow needles, melts at 103—104°, and dissolves readily in warm alcohol and benzene. The *benzoyl-compound*, $C_{35}H_{29}N_3O_4$, forms groups of yellowish needles, melts at 146°, and is readily soluble in alcohol, less so in ether.

Metamidophenyldiparamidotolylmethane, $C_{21}H_{23}N_3$, obtained by reducing the nitro-compound with tin and hydrochloric acid, crystallises in white plates, readily soluble in alcohol and ether. The *hydrochloride* forms white plates; the *platinochloride* crystallises in small, yellow plates, sparingly soluble in hot water.

α-Metanitrophenyldiparamidotolylmethane, $C_{21}H_{21}N_3O_2$, is prepared by the action of hydrochloric acid on metanitrobenzaldehyde and paratoluidine. It melts at 125—128°. The salts are decomposed by water.

Paranitrophenyldiparamidophenylisobutylmethane,

$$NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Bu{\cdot}NH_2)_2,$$

prepared from paranitrobenzaldehyde, paramidoisobutylbenzene sulphate, and strong sulphuric acid, crystallises in lustrous, yellow needles, melts at 125—126°, and is readily soluble in chloroform, benzene, and hot alcohol. The *hydrochloride* forms light yellow plates, readily soluble in hot alcohol; the *platinochloride* crystallises in yellow plates. The *acetyl-compound* crystallises in yellow grains, melts at 114°, and dissolves readily in benzene and in warm alcohol and ether. The *benzoyl-derivative* forms long, yellowish needles, melts at 125—126°, and is readily soluble in ether, benzene, chloroform, and boiling alcohol.

Metanitrophenyldiparamidophenylisobutylmethane, $C_{27}H_{33}N_3O_2$, forms light yellow plates, melts at 64—65°, and resembles the para-compound in solubility. The *benzoyl-derivative* crystallises from hot, aqueous alcohol in yellowish plates, melts at 113—114°, and is readily soluble in hot alcohol.

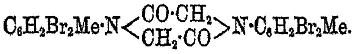
Paranitrophenyldiamidometaxylylmethane,

$$NO_2 \cdot C_6H_4 \cdot CH(C_8H_8 \cdot NH_2)_2,$$

prepared from paranitrobenzaldehyde (10 grams), unsymmetrical metaxylidine (10 grams), and sulphuric acid, crystallises in light yellow, lustrous, hair-like needles, melts at 89—90°, and dissolves readily in hot alcohol, in ether, benzene, and chloroform. The *hydrochloride* forms pale yellow, flat needles, dissolves readily in hot alcohol, and is decomposed by water. The *platinochloride* separates in yellow crusts. The *acetyl-derivative* forms small, light yellow grains melting at 88°; the *benzoyl-derivative* crystallises in voluminous, lustrous, pale yellow needles melting at 191—192°; both compounds dissolve easily in hot alcohol, less readily in ether.

Metanitrophenyldiamidometaxylylmethane, $C_{23}H_{25}N_3O_2$, crystallises from alcohol in pale yellow, slender plates, melts at 91—92°, and resembles the para-compound in solubility. The *hydrochloride* crystallises from alcoholic hydrochloric acid in pale yellow plates; the *platinochloride* forms a greyish-yellow, crystalline precipitate. The *acetyl-compound* separates from ether in small, light grey needles, melting at 131—132°; the *benzoyl-compound* forms voluminous, yellowish needles, and melts at 185—186°. N. H. M.

Halogen-substituted Acetamido-derivatives of the Aromatic Series and their derived Piazines. By P. W. ABENIUS and O. WIDMAN (*J. pr. Chem.* [2], 38, 296—312).—The substance of the formula $C_9H_7Br_2NO$, formed by digesting alcoholic potash (1 mol.) and bromacetodibromorthotoluidide (1 mol.) (see next Abstract); is very sparingly soluble in hot alcohol, but may be recrystallised from glacial acetic acid in colourless, hexagonal laminæ melting at 277°. It is an indifferent substance, soluble in neither alkalis nor strong mineral acids. Its constitution is most probably



$$C_6H_2Br_2Me \cdot N{<}{\genfrac{}{}{0pt}{}{CO \cdot CH_2}{CH_2 \cdot CO}}{>}N \cdot C_6H_2Br_2Me.$$

A. G. B.

Action of Bromine on Orthacetotoluidide at a High Temperature. By P. W. ABENIUS and O. WIDMAN (*J. pr. Chem.* [2], 38, 285–295).—*Bromacetodibromorthotoluidide*, $C_6H_2Br_2Me \cdot NH \cdot CO \cdot CH_2Br$, is obtained when orthacetotoluidide (10 grams) is heated at 160° and bromine (32 grams) added drop by drop; the product solidifies on cooling to a hard, brittle, black resin, which, when treated with chloroform, yields, besides an oil, the bromo-compound, as white, prismatic needles; the needles recrystallised from glacial acetic acid, melt at 207°; they are sparingly soluble in hot alcohol, more so in benzene. As this compound can be synthesised from bromacetic chloride and dibromorthotoluidine, its constitution is as expressed by the above formula. If it is digested for an hour with alcoholic potash (in mol. proportion), it loses a molecule of hydrogen bromide, and a sparingly soluble substance of the formula $C_9H_7Br_2NO$ separates; but when heated with a considerable excess of alcoholic potash in a reflux apparatus, it is decomposed with formation of dibromorthotoluidine and potassium bromacetate. *Dibromorthotoluidine platinochloride* crystallises in sparingly soluble, yellow needles.

Diacetyldibromorthotoluidide, $C_6H_2Br_2Me{\cdot}NAc_2$, prepared by heating dibromorthotoluidine for several hours with an excess of acetic anhydride, forms white needles, very soluble in alcohol, and melting at 88°. When only gently warmed with acetic anhydride, a substance melting at 200° is obtained, and is doubtless acetyldibromorthotoluidide, but has not yet been analysed.

Acetylglycolyldibromorthotoluidide, $C_6H_2Br_2Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}OAc$.—Perfectly pure bromacetyldibromorthotoluide (2 grams) is heated with acetamide (6 grams) at 150—170° until blackening begins; the mass is washed with water to remove excess of acetamide and hydrobromic acid, and the residual acetyl compound recrystallised from alcohol; it forms white needles melting at 172°. This substance was also obtained by heating bromacetodibromorthotoluidide with silver acetate. When heated with weak aqueous potash, it is dissolved and converted into *glycolyldibromorthotoluidide*, $C_6H_2Br_2Me{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}OH$, which crystallises as the solution cools in colourless laminæ, having curved edges; with a stronger solution of potash, the acetyl compound is converted into the laminæ without being dissolved. The laminæ crystallise from alcohol in slender, colourless needles, which melt at 182°, and are more easily soluble in weak alkali than in water; they are precipitated from the alkaline solution on neutralising it with hydrochloric acid. This compound is also obtained when the acetyl-derivative is heated with aqueous soda or with weak hydrochloric acid. A. G. B.

Phenylenediazosulphide. By P. JACOBSEN (*Ber.*, **21**, 3104—3107).—*Orthophenylenediazosulphide*, $C_6H_4{<}\substack{N\\S}{>}N$, is formed when the diazo-compound of diamidophenyl disulphide is boiled with water (Abstr., 1887, 961), and in much larger amount by the action of nitrous acid on amidophenyl mercaptan. It crystallises in plates, melts at 36—37°, has an agreeable, aromatic odour, and distils readily with steam; it is soluble in strong hydrochloric acid.

N. H. M.

Azo-xylenes, Diamido-dixylyls and Colouring Matters derived therefrom. By E. NÖLTING and T. STRICKER (*Ber.*, **21**, 3138—3149).—*Consecutive azortho-xylene*, $C_6H_3Me_2{\cdot}N{:}N{\cdot}C_6H_3Me_2$ [$Me_2 : N = 1 : 2 : 3$], is obtained when zinc-dust (20 grams) is gradually added to a boiling alcoholic solution (100 c.c.) of orthonitro-xylene (20 grams) and 32 per cent. soda (20 grams). After filtering and concentrating the solution, the product is washed with dilute hydrochloric acid and recrystallised several times from alcohol. It can also be obtained by oxidising the hydrazo-compound (see below) with ferric chloride or hydrogen peroxide in alcoholic solution. It crystallises in orange-yellow needles, melts at 110—111°, and is readily soluble in alcohol, ether, and benzene. The *hydrazo*-compound can be prepared by treating the azo-derivative with hydrogen sulphide or by reducing orthonitro-xylene as described above, employing 25 grams of zinc-dust. It crystallises from alcohol in colourless needles, melts at 139—141°, quickly oxidises on exposure to the air, and is soluble in the ordinary solvents—although not so readily as the azo-compound.

Unsymmetrical azortho-xylene, [Me_2 : N = 1 : 2 : 4], is prepared as described in the case of the isomeric compound, except that much more alcohol and very little soda must be employed, otherwise a red condensation product is formed (see below). It can also be obtained by reducing nitrortho-xylene with the theoretical quantity of sodium amalgam. It crystallises from alcohol, in which it is more sparingly soluble than the 1 : 2 : 3 compound, in red needles, and melts at 140—141°.

The *hydrazo*-compound, prepared by reducing an alcoholic solution of nitro-xylene with sodium amalgam or by treating the azo-compound with zinc-dust and soda, ammonium sulphide, or sodium amalgam, crystallises from alcohol in yellowish needles, melts at 106—107°, and is tolerably stable in the air.

Unsymmetrical azometaxylene, [Me_2 : N = 1 : 3 : 4], melting at 129°, can be obtained by reducing an alcoholic solution (300 c.c.) of the nitro-compound (25 grams) with zinc-dust (25—30 grams) and 32 per cent. soda (15 grams). (Compare Schultz, Abstr., 1884, 902.) The *hydrazo*-compound is obtained by boiling a mixture of alcohol (250 grams), nitro-xylene (30 grams), 32 per cent. soda (30 grams), and zinc-dust (40 grams), until the solution becomes almost colourless, and treating the crude product with hydrogen sulphide in alcoholic ammonia solution. It crystallises from alcohol in colourless needles, and melts at 120—122°.

Symmetrical azometaxylene, [Me_2 : N = 1 : 3 : 5], prepared by reducing an alcoholic solution (60 c.c.) of nitrometaxylene (10 grams) with zinc-dust (10 grams) and 32 per cent. soda (10 grams), crystallises in orange needles, is readily soluble in the usual solvents, and melts at 136—137°. The *hydrazo*-compound is prepared by treating nitrometaxylene (10 grams) with soda (3 grams) and zinc-dust (15 grams) in alcoholic solution (50 c.c.). It crystallises from alcohol in colourless needles, melts at 124—125°, and quickly oxidises on exposure to the air. It can also be obtained by reducing the azo-compound with ammonium sulphide.

Azoparaxylene, [Me_2 : N = 1 : 4 : 2], obtained by treating nitroparaxylene (20 grams) with zinc-dust (16—20 grams) and 32 per cent. soda (16 grams) in alcoholic solution (200 c.c.), crystallises in yellow needles and melts at 119°. The azo-xylene prepared by Werigo (*Zeit. f. Chem.* [2], 1, 312) is probably identical with this compound. The *hydrazo*-compound, prepared by reducing nitroparaxylene (30 grams) with 32 per cent. soda (25 grams) and zinc-dust (45 grams) in alcoholic solution (250 c.c.), crystallises from alcohol in colourless needles, melts at 145°, and is moderately stable in the air.

The hydrochlorides of the corresponding diamidodixylyls were prepared by heating the hydrazo-xylenes with moderately dilute hydrochloric acid, either alone or in alcoholic solution, adding excess of soda, extracting the base with ether, and saturating the dried ethereal solution with hydrogen chloride.

Hydrazometaxylene, [Me_2 : N = 1 : 3 : 4], by this treatment, yields chiefly azo-xylene and xylidine; the last-named compound is separated from the diamidodixylyl by distilling with steam. Hydrazortho-xylene, [Me_2 : N = 1 : 2 : 4], is hardly acted on at all when boiled with acids, and the hydrochloride of the corresponding diamidodixylyl was obtained by boiling an alcoholic solution of the azo-compound with hydrochloric acid and stannous chloride, separating the xylidine by distilling with steam and saturating an ethereal solution of the base with hydrogen chloride.

Nitrortho-xylene, [$Me_2 : NO_2 = 1 : 2 : 4$], yields a red, and nitrometa-xylene, [$Me_2 : NO_2 = 1 : 3 : 4$], a brownish-red condensation product when treated with alcoholic soda. The red compound is almost insoluble in ordinary solvents and, when reduced with stannous chloride and hydrochloric acid, is converted into dimethyldiamidostilbene. (Compare Bender and Schultz, Abstr., 1887, 268.)

All the bases obtained from the nitro-xylenes, after diazotising, yield with naphthionic acid α-naphthol-α-sulphonic acid and β-naphthol-disulphonic acid R, compounds which dye unmordanted vegetable fibres. The diphenyl-derivatives are reddish dyes with a more or less blue or yellowish shade, whereas the stilbene-derivative yields a bluish-violet dye with α-naphthol-α-sulphonic acid. The toluidines from meta- and para-nitrotoluene were also prepared; these bases yield red dyes with the above-named sulphonic acids. F. S. K.

Nitroso-derivatives of Resorcinol Azo-dyes. By S. v. KOSTANECKI (*Ber.*, **21**, 3109—3114).—*Nitrosophenylazoresorcinol*, $C_{12}H_9N_3O_3$, is readily obtained by adding a mixture of phenylazoresorcinol (1 mol.) dissolved in dilute alkali and sodium nitrite (1 mol.) to cooled, dilute sulphuric acid. The product is filtered, washed, and crystallised from alcohol. It separates in lustrous, brownish-red plates which, when heated at 168°, detonate; it dissolves sparingly in hot water, readily in benzene, and still more readily in chloroform; ether dissolves it sparingly. It dissolves in alkalis with yellowish-brown, and in strong sulphuric acid with olive-green colour, and yields an intense olive-green colour with iron mordants. Similar dyes were prepared from ortho- and para-toluidine, xylidine, pseudocumidine, meta- and para-nitraniline, amidoazobenzene, and naphthionic acid.

Nitrosopseudocumylazoresorcinol, $C_{15}H_{15}N_3O_3$, crystallises from chloroform in brown plates, decomposes when heated above 190°, and dissolves in alkalis and in strong sulphuric acid, yielding brownish-yellow and brownish-red solutions respectively.

When nitrosophenylazoresorcinol is reduced with tin and hydrochloric acid, diamidoresorcinol is formed.

Phenylazonitrosoresorcinol, $C_{12}H_9N_3O_3$, isomeric with nitrosophenylazoresorcinol, is obtained by adding nitrosoresorcinol dissolved in aqueous sodium carbonate to a solution of diazobenzene chloride cooled with ice. It crystallises from alcohol in golden plates which decompose at 225°. The solution in dilute soda is reddish-yellow; the sulphuric acid solution is olive-brown. When reduced, it yields the same diamidoresorcinol as that obtained from nitrosophenylazoresorcinol. N. H. M.

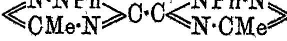
Isomeric Phenyldiazoresorcinols. By S. v. KOSTANECKI (*Ber.*, **21**, 3114—3119).—Symmetrical diamidoresorcinol, $C_6H_2(NH_2)_2(OH)_2$, is isolated in a manner similar to the consecutive derivative (preceding Abstract); it is identical with Typke's isodiamidoresorcinol (Abstr., 1883, 917). The *sulphate* (with 2 mols. H_2O) crystallises from very dilute alcohol in needles.

Symmetrical phenyldiazoresorcinol is formed when resorcinol (1 mol.) is added to a diazotised solution of aniline (2 mols.), and the whole poured into an excess of dilute alkali. Consecutive phenyldiazoresorcinol is obtained by adding a mixture of diazobenzene chloride (2 mols.) and resorcinol (1 mol.) to aqueous sodium acetate or sodium carbonate. The consecutive compound is best prepared as follows:—Aniline (2 mols.) is dissolved in dilute hydrochloric acid (5 mols.) and diazotised with sodium nitrite. When an excess of nitrous acid is no longer present, resorcinol (1 mol.) is added, the whole added to a dilute solution of sodium acetate or carbonate, and after being kept for some time, filtered, dried, and crystallised from a mixture of chloroform and alcohol. The isomerides have the properties already ascribed to them (Liebermann and v. Kostanecki, Abstr., 1884, 1146).

Phenylazoresorcinol is best prepared by adding resorcinol (1 mol.) to the diazotised solution of aniline hydrochloride (1 mol.), pouring the mixture in a thin-stream into an excess of dilute alkali, precipitating the phenylazoresorcinol with acid, and crystallising it from dilute alcohol. The theoretical yield is readily obtained.

N. H. M.

α-Ethylenephenylhydrazine. By O. BURCHARD and A. MICHAELIS (*Ber.*, **21**, 3202—3204).—*α-Ethylenephenylhydrazine*, $C_2H_4(NPh\cdot NH_2)_2$, is prepared by adding the calculated amount of ethylene bromide to finely powdered sodium phenylhydrazine covered with benzene. After 10 minutes the mixture becomes warm, and in a short time the reaction becomes so violent that the flask has to be cooled with ice water. The product is treated with water, and the benzene separated and extracted, first with very dilute hydrochloric acid, to remove any phenylhydrazine which is present, and then with strong hydrochloric acid. The base is precipitated from the aqueous solution with soda and crystallised twice from alcohol. It forms colourless prisms or plates, melts at 90°, and is readily soluble in hot alcohol and ether, and in dilute acids. It gradually reduces Fehling's solution when heated. The *hydrochloride*, $C_{14}H_{18}N_6,2HCl$, crystallises in needles of a silky lustre. When the base is treated with alcohol and then with acetaldehyde, heat is developed, and the condensation product, $C_2H_4(NPh\cdot N:CHMe)_2$, separates in long, white needles which melt at 82°. The corresponding *benzylidene-derivative* crystallises from hot glacial acetic acid in slender needles, melts at 193°, and is very sparingly soluble in ether and alcohol. N. H. M.

Di-phenylmethyltriazole. By J. A. BLADIN (*Ber.*, **21**, 3063—3065).—Di-phenylmethyltriazole,  $\left\langle\begin{matrix}N\cdot NPh\\ CMe\cdot N\end{matrix}\right\rangle C\cdot C\left\langle\begin{matrix}NPh\cdot N\\ N\cdot CMe\end{matrix}\right\rangle$, is obtained when cyanophenylhydrazine (Senf, Abstr., 1887, 929) is heated for a few minutes with excess of acetic anhydride. It crystallises from alcohol in colourless prisms, melts at 222—223°, and is readily soluble in chloroform, moderately so in alcohol, but only sparingly in benzene and ether, and insoluble in water. It is very stable, and is not decomposed when boiled with alcoholic potash or strong acids. The *hydrochloride*, $C_{18}H_{16}N_6,2HCl$, separates as a crystalline powder when concentrated hydrochloric acid is added to a boiling alcoholic solution of the base. It is almost insoluble in fuming hydrochloric acid, and is decomposed by water. The *platinochloride*, $C_{18}H_{16}N_6,H_2PtCl_6 + \frac{1}{2}H_2O$, crystallises in orange-yellow plates, becomes anhydrous at 125°, and is decomposed by water.

F. S. K.

Action of Sodium Hypobromite on Nitrogen-derivatives in the Benzene Series. By G. DENIGÈS (*Compt. rend.*, **107**, 662).—When an alkaline solution of sodium hypobromite is boiled for a few minutes with a solution of hippuric acid or a hippurate, gas is evolved, and a reddish-yellow precipitate is formed. Benzoic acid gives no reaction, and glycocine decolorises the hypobromite with evolution of nitrogen.

With sodium hypobromite, benzamide and benzonitrile give no reaction in the cold, but a kermes-red precipitate on heating. Aniline gives an orange precipitate, and the reaction is almost as delicate as that with hypochlorites. Methylaniline and dimethylaniline give a greenish-yellow precipitate in the cold and a red precipitate on heating. Toluidine behaves like aniline, but the precipitate is darker in colour. Anilides give no reaction in the cold, but a reddish precipitate is formed on boiling, and an odour of methyl cyanide can be perceived. Metaphenylenediamine, diamidobenzoic acid, and toluylenediamine yield maroon-red precipitates in both cold and hot solutions. Ferrocyanides, ferricyanides, and nitroprussides yield a precipitate of ferric hydroxide. Pyridine gives no reaction, and pure quinoline also gives no reaction, but if, as is frequently the case, it contains aniline, an orange precipitate is formed.

C. H. B.

Aromatic Derivatives of Oxamide and Oxamic Acid. By J. MAUTHNER and W. SUIDA (*Monatsh.*, **9**, 736—750; compare Abstr., 1886, 886; *Ber.*, **3**, 227).—When ethyl oxalate and orthotoluidine are heated together in molecular proportions, ethyl oxalorthotoluidate is formed, together with a little oxaltoluidide, the latter remaining undissolved on treatment with alcohol. On heating either alone or with acetic chloride, the free acid is converted into oxalorthotoluidide, which can also be obtained by heating together orthotoluidine (1 mol.) and anhydrous oxalic acid (2 mols.) at 220°. Oxalorthotoluidide melts at 207—208° and appears to be identical with the polyformotoluide described by Ladenburg.

Oxanilidediorthocarboxylic acid, $C_2O_2(NH{\cdot}C_6H_4{\cdot}COOH)_2$, may be obtained by the oxidation of oxalorthotoluidide with permanganate as well as by heating a mixture of anthranilic acid (2 mols.) and ethyl oxalate (1 mol.) at 140—150°. When sulphuric acid is added to an ammoniacal solution, the acid is thrown out in the form of a pulverulent precipitate. The copper salt, $C_{16}H_{10}N_2O_6Cu + CuO$, has a bright green colour; the silver salt, $C_{16}H_{10}N_2O_6Ag_2$, forms an insoluble, white precipitate.

Oxalxylidic acid, $C_8H_9{\cdot}NH{\cdot}CO{\cdot}COOH$, is formed by heating at 180—190° a mixture of α-amidometaxylene (1 mol.) and ethyl potassium oxalate (1 mol.). It crystallises in needles containing 1 mol. H_2O and melts at 128—129°. The silver salt, $C_{10}H_{10}AgNO_3$, and the calcium salt are both soluble in water and crystallise in needles. On heating the free acid, it is converted into *oxalxylidide*, $C_{10}H_{20}N_2O_2$, which crystallises from acetic acid and benzene in flat needles melting at 210°.

Oxal-ψ-cumidic acid, $C_9H_{11}{\cdot}NH{\cdot}CO{\cdot}COOH$, is prepared by heating at 200° a mixture of ψ-cumidine melting at 63° (1 mol.) and ethyl oxalate (1 mol.). It crystallises in needles containing 1 mol. H_2O and melting at 167°. The sodium salt, $C_{11}H_{12}NO_3Na + 3H_2O$, crystallises in scales; the potassium salt, $C_{11}H_{12}NO_3K,C_{11}H_{13}NO_3$, in needles; the calcium salt, $(C_{11}H_{12}NO_3)_2Ca + H_2O$, is a crystalline powder; the acid silver salt, $C_{11}H_{12}NO_3Ag,C_{11}H_{13}NO_3$, forms bundles of needles, and the normal salt, $C_{11}H_{12}NO_3Ag$, is a crystalline powder. On heating the free acid, it is converted into *oxal-ψ-cumidide*, which can be directly prepared by the action of anhydrous oxalic acid on the base, and crystallises from acetic acid in needles melting at 230°.

G. T. M.

Phthalimidine. By C. GRAEBE (*Annalen*, **247**, 288—301).—Phthalimidine is prepared by the reduction of phthalimide by tin and hydrochloric acid. The tin is precipitated from the crude product by strips of zinc, and the phthalimidine is deposited as the nitroso-compound on the addition of a concentrated solution of sodium nitrite. Nitrosophthalimidine is decomposed by strong hydrochloric acid, yielding a mixture of phthalimidine and its hydrochloride. The conversion of the nitroso-compound into phthalide and the properties of some of the phthalimidine-derivatives have already been described (Abstr., 1885, 167 and 979). Phthalimidine melts at 150°, and boils at 336—337° under 730 mm. pressure. It is freely soluble in alcohol, ether, and chloroform. On the addition of bromine to the solution in chloroform, the tribromide, $(C_8H_4NO)_2Br_3$, is deposited; it melts at 150° with decomposition. The *hydrochloride*, C_8H_7ON,HCl, *picrate* (m. p. 140°), and *aurochloride*, $(C_8H_7ON)_2,HAuCl_4$, are crystalline. *Phthalimidine silver*, C_8H_6ONAg, is deposited from ammoniacal solutions in crystals. *Acetylphthalimidine*, C_8H_6ONAc, melts at 151°, and does not yield a nitroso-derivative.

Nitrosophthalimidine is decomposed by sodium hydrogen sulphide, yielding *thiophthalide*, C_8H_6OS; this is freely soluble in alcohol and ether, melts at 60°, and is converted into a thio-derivative of hydroxymethylbenzoic acid by solution in alkalis and reprecipitation by acids. *Nitrophthalimidine* melts at 210°, and is deposited from alcoholic solution in pale yellow scales. It is soluble in alkalis: acids precipitate from the alkaline solution the compound $C_8H_8O_4N_2$; this is freely soluble in alcohol, ether, and in hot water. *Dinitrophthalimidine* melts at 195°.

W. C. W.

Substituted Phthalimidines. By C. GRAEBE and A. PICTET (*Annalen*, **247**, 302—306).—Methylphthalimide, $C_8H_4O_2NMe$, and methylphthalimidine, $C_8H_6O_4NMe$, have been previously described by the authors (Abstr., 1884, 1019). Methylphthalimide melts at 132° and boils at 285—286°. Ethyl phthalimide melts at 79° and boils at 282·5° under 726 mm. pressure. Ethyl phthalimidine melts at 45°. The *aurochloride*, $(C_{10}H_{10}ON)_2,HAuCl_4$, forms golden prisms melting at 145°. Phenyl phthalimidine, C_8H_6ONPh, prepared by reducing an alcoholic solution of phthalanil with tin and hydrochloric acid, is identical with Hessert's phthalidanil, obtained by the action of aniline on phthalide. W. C. W.

Action of Hypophosphorous Acid on Benzaldehyde. By J. VILLE (*Compt. rend.*, **107**, 659—661).—*Dihydroxybenzylenephosphinic acid*, $PO(CHPh·OH)_2·OH$, is obtained by the action of hypophosphorous acid on benzaldehyde, and crystallises in white, radiating lamellæ, which can be purified by solution in potassium hydroxide and reprecipitation by hydrochloric acid. It is only slightly soluble in water, chloroform, or benzene, but dissolves readily in ethyl alcohol or ether, and is still more soluble in methyl alcohol. With acids it forms crystallisable salts, and its solution has no reducing action on copper sulphate or ammoniacal silver solutions. It begins to melt at 165°, and forms a yellowish liquid, which if more strongly heated gives off hydrogen phosphide and leaves a bulky, carbonaceous residue. When heated in sealed tubes at 130° for several hours with dilute sulphuric acid, it yields benzaldehyde and phosphoric acid.

Dihydroxybenzylenephosphinic acid is monobasic. The *silver salt* forms a white, crystalline precipitate which blackens when exposed to light, and is insoluble in water and nitric acid, but dissolves readily in ammonia. The *ethyl salt* is almost insoluble in water, and is only slightly soluble in ether or chloroform, but it dissolves readily in ethyl alcohol, from which it crystallises in brilliant prisms. It is slowly saponified by cold solutions of potassium hydroxide, and if the liquid is acidified, the free acid separates in crystals. With hot potassium hydroxide, the reaction is more complex, and benzaldehyde and phosphoric acid are obtained.

When the ethyl salt is treated with acetic chloride, it yields the compound $PO(CHPh·OAc)_2·OEt$, a viscous, transparent substance, soluble in alcohol or ether, from which it separates in very white crystals. The acetyl-derivative is slowly saponified by potash in the cold, and if the product is acidified, dihydroxybenzylenephosphinic acid separates, and the solution contains acetic acid. With hot potash, the products are benzaldehyde, phosphates, and acetates.

C. H. B.

On Mono- and Di-nitroparazobenzoic Acids. By Madame A. RODSIANKO (*J. Russ. Chem. Soc.*, 1888, **20**, 18—29).—The action of nitric acid on parazobenzoic acid was studied, and the product compared with the nitro-compound obtained from azobenzoic acid by Zinin. Solid nitrotoluene is oxidised by chromic mixture to paranitrobenzoic acid, and this on treatment with sodium amalgam yields parazobenzoic acid; the latter, after having been dried between blotting paper, still contains 30—35 per cent. of water. It is treated with 16 times its weight of nitric acid of sp. gr. 1·535, gradually warming the mixture, until the temperature reaches 79°, and all the acid is dissolved. On adding water, 90—94 per cent. of a solid product is precipitated. This is washed with water, and recrystallised successively from glacial acetic acid, and several times from alcohol. The product consists of *nitrazobenzoic acid*, $C_{14}H_9(NO_2)N_2O_4$, and forms a pale yellow, crystalline powder consisting of rhombic scales. It is highly electric. It does not melt, but decomposes at 270°. It is insoluble in water, ether, and benzene, soluble in acetic acid and in 26·2 parts of hot, and 280·4 parts of cold alcohol. It forms two series of salts; the acid salts are stable, but the normal salts are decomposed by water, with formation of acid salts. The normal potassium salt, $K_2C_{14}H_7(NO_2)N_2O_4 + 3H_2O$, loses its water at 120°, and is decomposed by carbonic acid, yielding the acid salt. The calcium salt, $CaC_{14}H_7(NO_2)N_2O_4$, and the barium and silver salts have an analogous composition. The ethyl salt, obtained from the silver salt and ethyl iodide, forms pale yellow, rhombic scales melting at 98°.

Dinitroparazobenzoic acid is obtained when 30 parts of nitric acid of sp. gr. 1·535 is employed for 1 part of azobenzoic acid, and the mixture heated nearly to the boiling point. It is purified like the mononitro-acid, and forms tufts of slender yellow needles. It decomposes at 257° without melting. Like the mononitro-compound, it is soluble only in acetic acid and in 16·5 parts of hot, and 160·3 parts of cold alcohol. Its stable normal salts have a composition corresponding with that of the potassium salt, $K_2C_{14}H_6(NO_2)_2N_2O_4 + 4H_2O$. The calcium and barium salts contain 5 mols. H_2O; the silver salt is anhydrous. The ethyl salt forms slender, yellow, silky needles melting at 128°. Finally, azobenzoic acid, obtained by the decomposition of nitrobenzil (Zinin), was treated with nitric acid, and a product obtained which proved to be identical with the mononitroparazobenzoic acid, described above. The two azobenzoic acids are therefore identical. B. B.

Reissert's Pyranilpyroïc Acid. By R. ANSCHÜTZ (*Ber.*, **21**, 3252—3256); A. REISSERT (*Ber.*, **21**, 3257).—Anschütz's paper is a reply to one of Reissert's (Abstr., 1888, 954). Reissert mentions that the most important evidence in favour of his views depends on the knowledge of the constitution of anilsuccinic and β-anilpropionic acids, and that this point is not discussed by Anschütz. N. H. M.

Nitro-derivatives of Isophthalic Acid. By A. CLAUS and S. WYNDHAM (*J. pr. Chem.* [2], **38**, 313—320).—*Dinitroisophthalic acid* is formed when isophthalic acid (5 parts) is heated with fuming nitric acid (1 part) in a sealed tube for six hours at 150—180°. It is but little soluble in cold water, more freely in hot water, and in alcohol and ether; it forms colourless needles or short prisms, arranged in papillary aggregates, and containing 5 mols., H_2O, half of which is lost over sulphuric acid; the anhydrous acid melts at 215° (uncorr.). The *sodium* and *potassium* salts (2 mols. H_2O), the *barium* salt

(7 mols. H_2O), the *calcium* and *magnesium* salts (4 mols. H_2O), and the *lead* and *silver* salts are described. As the same dinitro-compound can be obtained by nitrating symmetrical nitroisophthalic acid, one of the nitro-groups is in the position 5, but the position of the other remains an open question.

Diamidoisophthalic acid, $C_6H_2(NH_2)_2(COOH)_2$, obtained by reducing the above acid, crystallises with 1½ mol. H_2O in shining, flat needles, of a very light-brown tint, becoming darker on exposure to light, and not melting below 300°; its aqueous solution deposits a black tarry matter when incautiously evaporated, and acquires a mushroom-like odour after a time.

Dibromisophthalic acid, obtained when symmetrical nitroisophthalic acid is heated with bromine for several hours at 300° in a sealed tube, crystallises in colourless needles melting at 155° (uncorr.), sparingly soluble in water, freely in alcohol and ether, and subliming with the same crystalline form. The *calcium* and *silver* salts form anhydrous crystals.

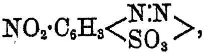
Nitroisophthalic acid ($NO_2 : COOH : COOH = 4 : 1 : 3$), may be obtained by oxidising 4-nitrometatoluic acid with potassium permanganate; it crystallises with 3 mols. H_2O in small white needles, easily soluble in hot water, in alcohol and ether. The anhydrous acid melts at 246° (uncorr.); its *sodium*, *potassium* (1 mol. H_2O), *barium* (4 mols. H_2O), *calcium* (½ mol. H_2O) and *magnesium* (6 mols. H_2O), *lead* and *silver* (7½ mols. H_2O) salts are all described. A. G. B.

Phenylglycinorthocarboxylic Acid: Glycocine-derivatives. By J. MAUTHNER and W. SUIDA (*Monatsh.*, 9, 727—735).—Instead of employing 2 mols. of the base to one of chloracetic acid in the preparation of glycocine-derivatives, as in the ordinary method, the authors replace the second molecule of the base, which is needed to combine with the hydrochloric acid liberated, by an equivalent quantity of a metallic carbonate, whereby not only is material saved, but the reaction is hastened.

Phenylglycinorthocarboxylic acid, $COOH{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}COOH$, is prepared by boiling a mixture of anthranilic acid (25 grams) chloracetic acid (20·6 grams), sodium carbonate (32·8 grams) and water (1 litre) for several hours, the water as it evaporates being replaced. After cooling, the product is supersaturated with hydrogen chloride acid and allowed to remain for one day, when the acid separates as a bright-yellow, crystalline powder which melts with frothing at 207°. It dissolves readily in alcohol, acetic acid, and ether, but is insoluble in benzene and chloroform. The acid potassium salt, $C_9H_8NO_4K$, crystallises from dilute alcohol in microscopic scales. The calcium salt is anhydrous, and furnishes aniline on distillation. The barium salt, $C_9H_7NO_4Ba + 2H_2O$, crystallises in needles; the silver salt, $C_9H_7NO_4Ag_2$, is insoluble in water, and the ethyl salt, $C_9H_8NO_4Et$, forms an oil which crystallises on standing.

If chloracetic acid (50 grams) soda (53 grams) and excess of ammonia are boiled for 7—8 hours, glycocine is formed (16 to 18 per cent. of theory). If the ammonia be omitted, glycollic acid (yield 75 per cent. of theory) is the product. G. T. M.

Orthonitranilinesulphonic Acid and some of its Derivatives. By R. NIETZKI and Z. LERCH (*Ber.*, **21**, 3220—3223).—Orthonitranilinesulphonic acid (Goslich, Abstr., 1876, i, 929) is prepared by treating acetanilide (1 part) with fuming sulphuric acid, containing 18 to 20 per cent. of anhydride (3 parts), and ordinary sulphuric acid (2 parts). The calculated amount of nitric acid, previously mixed with an equal volume of sulphuric acid, is then gradually added, the whole being kept at 0°. The product is poured on to a little ice, when it solidifies to a mass of yellow needles. It is extremely soluble in water, less so in alcohol or in dilute sulphuric or hydrochloric acid. When the potassium salt is boiled with an excess of potash for a long time, ammonia is evolved, and the potassium salt, $OK\cdot C_6H_3(NO_2)\cdot SO_3K$ (Kolbe and Graebe, *Annalen*, **147**, 76), is obtained.

Nitrodiazobenzenesulphonic acid,  $NO_2\cdot C_6H_3<\substack{N:N\\SO_3}>$, obtained by treating the aqueous solution of the amido-acid with hydrochloric acid and potassium nitrite, crystallises in slender, light-yellow needles, dissolves sparingly in water, and detonates rather violently when heated.

Orthophenylenediaminesulphonic acid, $C_6H_3(NH_2)_2\cdot SO_3H$, is formed when the nitranilinesulphonic acid is reduced with tin and hydrochloric acid. When exposed to air, it becomes greenish-blue, and gives a reddish-brown colour with ferric chloride. The acid is not identical with Sachsse's acid (this Journal, 1877, ii, 751), but possibly is with the one prepared by Post and Hartung (Abstr., 1880, 394).

Orthonitrophenylhydrazineparasulphonic acid,

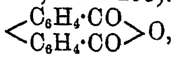
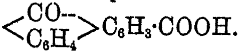
$$NH_2\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3H,$$

is obtained by adding orthonitrodiazobenzenesulphonic acid to a well-cooled, strongly acid stannous chloride solution. It dissolves in water and in aqueous alkalis and alkaline carbonates. When reduced with hot acid stannous chloride solution, the corresponding *amidohydrazinesulphonic acid* is formed. The *hydrochloride* crystallises in plates, and dissolves readily in water, but only sparingly in strong hydrochloric acid. N. H. M.

The Sulphonic Acid of Methyl Phenylcarbamate. By E. NÖLTING (*Ber.*, **21**, 3154—3155).—The compound obtained by Hentschel (Abstr., 1885, 792) by treating methyl phenylcarbamate with fuming sulphuric acid, is probably the acid,

$$COOMe\cdot NH\cdot C_6H_4\cdot SO_3H.$$

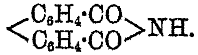
This substance can also be obtained by adding soda (1 mol.) to a warm aqueous solution of sodium sulphanilate (1 mol.), and methyl chloroformate (1 mol.). The amidosulphobenzoic acid prepared by Hentschel (Abstr., 1884, 1016) is probably sulphophenylcarbamic acid, $SO_3H\cdot C_6H_4\cdot NH\cdot COOH$. When methyl phenylcarbamate is heated at about 260° with lime, aniline, monomethylaniline, dimethylaniline, and carbanilide are formed. F. S. K.

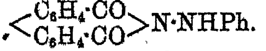
Diphenic Anhydride and Orthodiphenyleneketonecarboxylic Acid. By C. Graebe and C. Aubin (*Annalen*, **247**, 257—288).—Diphenic acid is convered into diphenic anhydride,  $<\substack{C_6H_4\cdot CO\\ C_6H_4\cdot CO}>O$, by the action of acetic chloride or acetic anhydride (Abstr., 1887, 589), also by boiling with stannic chloride or phosphorus trichloride, or by the action of phosphorus pentachloride containing oxychloride at 120°. Concentrated sulphuric acid, zinc chloride, and an excess of boiling phosphorus oxychloride convert diphenic acid into orthodiphenyleneketonecarboxylic acid,  $<\substack{CO\text{--}\\ C_6H_4}>C_6H_3\cdot COOH$.

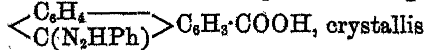
Monomethyl and ethyl diphenates are prepared by boiling diphenic anhydride with methyl or ethyl alcohol. They crystallise in colourless plates, dissolve freely in alcohol, and distil without decomposition. The ethyl salt melts at 88° and the methyl salt at 110°. *Diphenic chloride*, $C_{14}H_8Cl_2$, prepared by the action of phosphorus pentachloride on the anhydride at 180°, is a crystalline substance soluble in benzene, ether, and acetic acid. It melts at 93—94°, and distils without decomposition. On reduction, diphenic chloride yields phenanthraquinol, which changes into phenanthraquinone by oxidation.

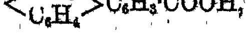
Diphenic anhydride is converted into the *aminic acid*,

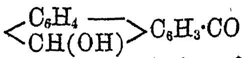
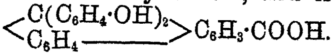
$$COOH\cdot C_6H_4\cdot C_6H_4\cdot CONH_2,$$

by boiling it with ammonia. This substance melts at 193° and decomposes on distillation, yielding *diphenimide*,  $<\substack{C_6H_4\cdot CO\\ C_6H_4\cdot CO}>NH$. The imide is deposited from hot alcohol in colourless needles, soluble in chloroform. It melts at 219—220°. Warm strong ammonia converts the imide into *diphenamide*, $NH_2\cdot CO\cdot C_6H_4\cdot C_6H_4\cdot CO\cdot NH_2$. The amide melts at 208—209°, and is insoluble in sodium hydroxide.

Phenylhydrazine unites with diphenic anhydride, forming *anilidodiphenamic acid*, $C_{20}H_{16}O_3N_2$, melting at 174°. At 200°, the acid begins to lose water and slowly changes into anilidodiphenimide,  $<\substack{C_6H_4\cdot CO\\ C_6H_4\cdot CO}>N\cdot NHPh$. This substance melts at 150°, and is insoluble in alkaline carbonates.

The salts of orthodiphenylcarboxylic acid have been previously described (Abstr., 1887, 589). The acid yields a mono- and a trichloride on treatment with phosphorus pentachloride. The *monochloride*, $C_{14}H_7O_2Cl$, melts at 128°, and the trichloride at 95°. The trichloride dissolves in alcohol, and the solution deposits crystals of the composition $<\substack{C_6H_4\\ CCl_2}>C_6H_3\cdot COOEt$. Reduction with zinc and acetic acid converts the trichloride into fluorenecarboxylic acid. The *acetoxime* melts at 263°, and decomposes at a high temperature. The *hydrazone*,  $<\substack{C_6H_4\text{———}\\ C(N_2HPh)}>C_6H_3\cdot COOH$, crystallises in yellow needles or prisms, and is soluble in alcohol and ether. It melts at 205° and decomposes at 210°.

Orthofluorenecarboxylic acid,  $<\substack{CH_2\\ C_6H_4}>C_6H_3\cdot COOH$, melts at 175°, and dissolves freely in ether, alcohol, and acetic acid. The methylic salt melts at 64°.

Hydroxyfluorenecarboxylic acid,  $<\genfrac{}{}{0pt}{}{C_6H_4}{CH(OH)}>C_6H_3 \cdot COOH$, prepared by the action of zinc-dust on an ammoniacal solution of diphenyleneketonecarboxylic acid, is soluble in alcohol, ether, benzene, chloroform, and in hot water. It melts at 203°. The substance which Graebe and Mensching (Abstr., 1880, 812) described as a phthaleïn of diphenic acid, is a condensation product of phenol and diphenyleneketonecarboxylic acid, and is probably represented by the formula  $<\genfrac{}{}{0pt}{}{C(C_6H_4 \cdot OH)_2}{C_6H_4}>C_6H_3 \cdot COOH$.

On heating a mixture of resorcinol and stannic chloride at 115°, a yellowish-brown crystalline powder is produced. The solution in alkalis has a yellowish-red colour and exhibits an intense green fluorescence.

W. C. W.

Nitro-derivatives of Tetramethyldiamidodiphenylmethane. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, 7, 226—235).—*Tetramethyldiamidodiphenylmethane* was prepared by heating methylal and dimethylaniline with zinc chloride. It melts at 90°, gives a violet compound with trinitrobenzene melting at 114°, and a dark red compound with metadinitrobenzene melting at 74°, the first containing equal molecular proportions, the second 2 mols. of the amine to one of dinitrobenzene. Added in acetic acid solution to nitric acid (sp. gr. 1·48—1·5), it is converted into *tetranitrodimethyldinitramidodiphenylmethane*, $CH_2[C_6H_2(NO_2)_2 \cdot NMe \cdot NO_2]_2$. This nitramine is a yellow, crystalline substance, which darkens in colour at 210° and decomposes at 217—220°. It is nearly insoluble in alcohol, ether, petroleum, carbon bisulphide, and chloroform, dissolves readily in acetic acid and acetone, but is best recrystallised from nitric acid. Precipitated as a white powder from the nitric acid solution by the addition of water, and boiled with 12·5 per cent. aqueous potash, it gives a brown solution which on evaporation was found to give off methylamine. When boiled with phenol, it gives *tetranitrodimethyldiamidodiphenylmethane*, an orange-coloured compound melting with decomposition at 250°. It is slightly soluble in alcohol, petroleum, and benzene, but more soluble in acetone, acetic acid, chloroform, and ethyl acetate. When treated with nitric acid, it is reconverted into the nitramine.

The latter, when oxidised with chromic anhydride, yields a compound exactly resembling that obtained by the nitration of tetramethyldiamidobenzophenone; on treatment with phenol, this gives a tetranitrodimethyldiamidobenzophenone melting at 225°. Admitting the formula which the author proposed for the nitramine derived from benzophenone, that of the one now in question will be

$$NO_2 \cdot \overset{4}{N}Me \cdot C_6H_2\overset{3,5}{(NO_2)_2} \cdot \overset{1}{C}H_2 \cdot C_6H_2\overset{2,6}{(NO_2)_2} \cdot \overset{4}{N}Me \cdot NO_2.$$

The compound obtained from this by boiling with phenol was also oxidised in acetic acid solution with chromic anhydride, and gave a *tetranitrodiamidobenzophenone*, crystallising in small yellow needles from acetic or phenol, and melting with decomposition at 250—260°.

H. C.

Action of Primary Aromatic Amines on Benzil. By F. X. BANDROWSKI (*Monatsh.*, 9, 685—694; compare Voigt, Abstr., 1885, 1067).—Benzil forms condensation products with the amines when they are heated together in open vessels at 100—150°. With aniline and orthotoluidine, only monosubstituted, but with paratoluidine and α-naphthylamine, a mixture of both mono- and di-substituted compounds were obtained. All the compounds of benzil described below are characterised by not forming salts with dilute acids and by the ease with which they are reconverted into their generators.

Anilbenzil, $COPh\cdot CPh:NPh$, melts at 105°, and gives characteristic colours with alcohohic potash (violet) and with cold concentrated sulphuric acid (blood-red, turning to green).

Orthotolilbenzil, $COPh\cdot CPh:N\cdot C_7H_7$, crystallises from alcohol in yellow plates which melt at 104°, and readily dissolve in ether and benzene.

Paratolilbenzil crystallises in yellow prisms melting at 116—117°.

Paraditolilbenzil, $C_7H_7\cdot N:CPh\cdot CPh:N\cdot C_7H_7$, is a bright yellow, crystalline powder melting at 161°, and more soluble in alcohol than paratolilbenzil.

α-Naphthilbenzil, $COPh\cdot CPh:N\cdot C_{10}H_7$, crystallises from alcohol in golden-yellow needles melting at 138—139°. It dissolves readily in benzene, less readily in ether, and with difficulty in light petroleum.

Di-α-naphthilbenzil, $C_{10}H_7\cdot N:CPh\cdot CPh:N\cdot C_{10}H_7$, is insoluble in alcohol, but crystallises from a mixture of benzene and light petroleum in dark yellow needles melting at 218—219°.

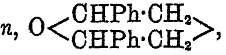
Orthotolilbenzoïn, $OH\cdot CHPh\cdot CPh:N\cdot C_7H_7$, is obtained by heating together equal quantities of benzoïn and orthotoluidine for three-quarters of an hour at 150°. It crystallises from alcohol in light yellow needles, readily soluble in ether, and melts at 141°.

G. T. M.

Derivatives of Ethyl Phenacylbenzoylacetate. By S. KAPF and C. PAAL (*Ber.*, 21, 3053—3063). The compound melting at 142—145°, obtained together with benzoic and benzylpropionic acid by hydrolysing ethyl phenacylbenzoylacetate (compare Abstr., 1888, 839) is diphenacyl (diphenyl ethylene diketone) (compare Nölting and Kohn, Abstr., 1886, 349; Claus and Werner, Abstr., 1887, 827; and Hollemann, Abstr., 1888, 275). It can be obtained by mixing ethyl phenacylbenzoylacetate (1 mol.) with a small quantity of alcohol, adding an 8 per cent. aqueous solution of potash (1½ mol.) and keeping the mixture for 8 to 10 days at the ordinary temperature; the whole is then filtered, the residue extracted with cold ethyl acetate to remove the unchanged ethereal salt, and recrystallised from alcohol or from a mixture of benzene and light petroleum. The yield is 20—25 per cent. of the ethereal salt employed.

Diphenacyldihydrazone, $C_2H_4(CPh:N_2HPh)_2$, prepared by boiling the diketone with phenylhydrazine, crystallises from alcohol in slender, colourless needles, melts at 180° with decomposition, and is readily soluble in ether, benzene, and hot glacial acetic acid. The impure compound is unstable, especially in the light. The *dioxime*, $C_2H_4(CPh:N\cdot OH)_2$, prepared by boiling a dilute alcoholic solution of the diketone with hydroxylamine, crystallises from dilute alcohol in colourless needles or plates, melts at 203—204°, and is readily soluble in glacial acetic acid, alcohol, ether, alkalis, and mineral acids, but sparingly in benzene and light petroleum.

$\alpha\alpha'$-Diphenylfurfuran (*loc. cit.*) is obtained when the diketone is heated at 130—150° with concentrated hydrochloric acid. It gives a dark grey coloration with isatin and sulphuric acid, and dissolves in concentrated sulphuric acid, forming a green solution which, on heating, changes to reddish-brown with a bluish-green fluorescence. Diphenacyl gives the same reaction with concentrated sulphuric acid.

Diphenyltetrahydrofurfuran,  $O<\begin{matrix}CHPh\cdot CH_2\\CHPh\cdot CH_2\end{matrix}>$, prepared by treating a hot alcoholic solution of diphenylfurfuran with sodium, is a colourless, viscid oil boiling at 230—232°. It is insoluble in water but mixes with most of the ordinary solvents in all proportions.

2 : 5 *Diphenylthiophen*, $C_4SH_2Ph_2$, obtained by heating diphenacyl (1 part) with phosphoric sulphide ($1\frac{1}{2}$ parts) at 160—186°, crystallises from alcohol or acetic acid in yellowish or colourless plates, melts at 152—153°, is readily soluble in most of the ordinary solvents and distils unchanged. It shows the indophenin and Laubenheimer's reaction.

When ethyl phenacylbenzoylacetate is heated at 150—200° with glacial acetic acid and excess of phosphoric sulphide, an acid melting at 216°, probably diphenylthiophencarboxylic acid, is obtained.

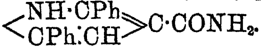
Ethyl $\alpha\alpha$*-diphenylfurfuran-*β*-carboxylate*, $C_4HPh_2O\cdot COOEt$, is obtained when finely-divided ethyl phenacylbenzoylacetate is boiled with alcohol and excess of moderately concentrated hydrochloric acid. It separates from dilute alcohol in large crystals.

Phenylacetylenebenzoylacetic acid (*loc. cit.*) yields a monobromo-substitution product which crystallises in colourless needles melting at 200°. When the acid is treated with phosphoric chloride in chloroform or carbon bisulphide solution, and the product poured into well-cooled methyl alcohol, it yields a *methyl* salt which crystallises in orange needles and contains chlorine. A yellow, crystalline *hydrazone*, $C_{29}H_{40}N_4O$, is formed when the acid is warmed with phenylhydrazine; it melts at about 100°, is insoluble in water and resinifies when treated with most ordinary solvents. The acid also combines with hydroxylamine.

Ethyl diphenylpyrroline-β*-carboxylate*,

$$C_4NH_2Ph_2\cdot COOEt\ [= 2:5:3],$$

is obtained when ethyl phenacylbenzoylacetate is heated with ammonium acetate and glacial acetic acid. It crystallises from acetic acid in colourless needles, melts at 159°, and distils unchanged when heated in small quantities. It is readily soluble in alcohol, ether, benzene, and glacial acetic acid, sparingly in light petroleum, and insoluble in water. It dissolves in warm, concentrated sulphuric acid with a reddish-brown coloration which changes to reddish-violet with a blue fluorescence when the solution is heated more strongly.

2 : 5-Diphenylpyrrolinecarboxylic acid (*loc. cit.*) melts at 216°. The compound described as ethyl αα-diphenylpyrroline-β-carboxylate (*loc. cit.*) is the *amide*,  $<\begin{matrix}NH\cdot CPh\\CPh{:}CH\end{matrix}>C\cdot CONH_2$. αα-Diphenylpyrroline can be obtained by boiling ethyl diphenylpyrrolinecarboxylate with alcoholic potash, by boiling diphenacyl with ammonium acetate and glacial acetic acid, and by heating the diketone at 150—160° with alcoholic ammonia. It is also obtained by distilling diphenylpyrrolecarboxylic acid over heated lime, but considerable decomposition takes place (compare Baumann, Abstr., 1887, 735, and Holleman, *loc. cit.*). It gives the same coloration with concentrated sulphuric acid as the ethereal salt described above.

Ethyl triphenylpyrrolinecarboxylate,

$$C_4NHPh_3{\cdot}COOEt\ [Ph_3 : COOEt = 1 : 2 : 5 : 3],$$

prepared by boiling ethyl phenacylbenzoylacetate with aniline and glacial acetic acid, crystallises from glacial acetic acid in yellowish, slender needles, melts at 169—170°, and is only sparingly soluble in most ordinary solvents.

Triphenylpyrrolinecarboxylic acid, $C_4NHPh_3{\cdot}COOH$, prepared by boiling the ethereal salt with alcoholic potash, crystallises from glacial acetic acid in needles, melts at 273°, and is rather sparingly soluble in most of the ordinary solvents. It sublimes with only slight decomposition and gives a reddish-brown solution when heated with concentrated sulphuric acid.

2 : 5-Triphenylpyrroline (compare Baumann, *loc. cit.*) and a compound melting at 140—142° are obtained when the preceding compound is distilled over heated lime. The substance melting at 140—142° crystallises in colourless needles or plates, and has the same composition as triphenylpyrroline. F. S. K.

Derivatives of α-β-Dichloronaphthalene. By P. Hellström (*Ber.*, **21**, 3267—3271).—*Dinitrodichloronaphthalene*, $C_{10}H_4Cl_2(NO_2)_2$, is prepared by the action of a mixture of fuming nitric and strong sulphuric acids (equal parts) on dichloronaphthalene. It crystallises in spherical aggregates of bright yellow, slender, flat needles, melts at 169·5°, and dissolves very sparingly in ether, very readily in boiling glacial acetic acid. When distilled with phosphorus pentachloride, a compound, possibly hexachloronaphthalene, is obtained which crystallises in long, bright yellow needles melting at 135—136°.

α-β-Dichloronaphthaquinone, $C_{10}H_4O_2Cl_2$, obtained by adding a solution of α-β-dichloronaphthalene in glacial acetic acid to a solution of chromic acid in glacial acetic acid (Guareschi, *Ber.*, **19**, 1154), melts at 181°, sublimes in long, yellow needles, and is rather sparingly soluble in alcohol. It yields with hydroxylamine a compound which crystallises in reddish-brown needles, and carbonises at 215°. When a solution of the quinone is treated with aniline, *dichloranilidonaphthaquinone*, $C_{10}H_3O_2Cl_2{\cdot}NHPh$, is formed. It is a red, crystalline substance, melts at 254—255°, and is very sparingly soluble in glacial acetic acid, less soluble in alcohol; it sublimes in carmine-red needles with a greenish-bronze lustre.

The above results show that α-β-dichloronaphthalene is not identical with the so-called α-dichloronaphthalene. N. H. M.

Disubstituted Naphthalenes from the Isomeric Chlorophenylparaconic Acids. By H. Erdmann and R. Kirchhoff (*Annalen*, **247**, 366—380).—The isomeric chlorophenylparaconic acids yield chlor-α-naphthols on distillation, just as phenylparaconic acid yields α-naphthol (Abstr., 1884, 906). The naphthols are converted into the corresponding dichloronaphthalenes by the action of phosphorus pentachloride. Metachlorophenylparaconic acid yields the 1 : 1'-chloronaphthol.

Ortho- and para-chlorobenzaldehydes are prepared by converting the chlorotoluenes into chlorobenzal chlorides, and decomposing the product by the action of anhydrous oxalic acid at 160°. The metachlorobenzaldehyde is obtained from metamidobenzaldehyde. When the chlorobenzaldehydes are heated at 120—140° with succinic anhydride and potassium acetate in molecular proportion, chlorophenylparaconic acids are produced.

The *ortho*-acid, $C_{11}H_9ClO_4 + 1\frac{1}{2}H_2O$, crystallises in needles, and melts at 146—147°. 100 parts of boiling water dissolve 1·4 parts of the acid. The *para*-acid crystallises with $\frac{1}{2}$ mol. H_2O. 1 part by weight of the acid dissolves in 100 parts of water at 100°, and in 500 at 16°. The acid melts at 119—120°. The *meta*-acid forms prisms and melts at 160—161°.

Chloronaphthol, [Cl : OH = 4 : 1'], crystallises in plates and melts at 131·5°. The acetate melts at 53°, and the picrate at 160°. Both salts are crystalline.

The 2 : 1'-chloronaphthol melts at 123°, and the picrate at 139°. The acetate is an uncrystallisable oil. By the action of ammonium calcium chloride at 260°, the chloronaphthol is converted into chloronaphthylamine. The hydrochloride melts at 235—239°, and yields a crystalline precipitate with platinum chloride. 3 : 1'-chloronaphthol crystallises in prisms, and melts at 94°. The acetate forms rhombic plates, and melts at 47°. The picrate crystallises in needles, and melts at 165°.

The three dichloronaphthalenes obtained by the action of phosphorus pentachloride on the chloronaphthols have the following melting points:—

Cl : Cl = 4 : 1' melts at 107°, and is identical with 1 : 4' dichloronaphthalene; 2 : 1' dichloronaphthalene melts at 61·5°; and 3 : 1' at 48°. The two last compounds have been previously described by Cleve and others. W. C. W.

Dimethyl-α-Naphthylamine and Diethyl-α-Naphthylamine. By P. Friedländer and P. Welmans (*Ber.*, **21**, 3123—3130).—Dimethyl-α-naphthylamine (Hantzsch, Abstr., 1880, 813) boils at 272—274° (uncorr.), and is very strongly refractive.

Amidodimethylnaphthylamine, $NH_2{\cdot}C_{10}H_6{\cdot}NMe_2$, is prepared by reducing the nitroso-compound, or from the azo-derivative. It dissolves readily in the usual solvents and in dilute mineral acids, and separates from the aqueous solution as an oil; it quickly becomes resinous when exposed to air. The *acetyl-derivative* crystallises in pointed plates, melts at 194—195°, and dissolves readily in alcohol and glacial acetic acid, sparingly in ether.

Nitrosodimethyl-α-naphthylamine, $NO{\cdot}C_{10}H_6{\cdot}NMe_2$, is obtained by adding a strong solution of sodium nitrite (7 grams) to dimethylnaphthylamine (17 grams) dissolved in hydrochloric acid (30 c.c.) in presence of ice. The solid product is freed from adhering liquid by suction, dissolved in cold alcohol, and precipitated with ether. The substance, which is probably the hydrochloride of the base, is readily soluble in a little water, but is decomposed when the solution is diluted. The free base is precipitated as an oily precipitate which gradually solidifies when sodium carbonate is added to the solution of the hydrochloride. It quickly decomposes into dimethylamine and nitrosonaphthol.

Dimethylnaphthylaminecarboxylic acid, $COOH{\cdot}C_{10}H_6{\cdot}NMe_2$, prepared by heating the base (2 mols.) with carbonyl chloride (1 mol.) at 60—70° for three to four hours, crystallises from alcohol in white, pointed needles melting at 163—165°. The *platinochloride*,

$$(COOH{\cdot}C_{10}H_6{\cdot}NMe_2)_2,H_2PtCl_6,$$

crystallises in yellow needles. The salts of the alkalis are readily soluble, and do not crystallise well.

Bromodimethylnaphthylamine hydrobromide crystallises from water in presence of hydrogen bromide in quadratic plates of a silvery lustre. The *free base* is a strongly refractive oil which boils at 260° with decomposition.

Dimethylnaphthylaminesulphonic acid, $SO_3H{\cdot}C_{10}H_6{\cdot}NMe_2$, prepared by heating the base with sulphuric acid (4 parts) at 150°, crystallises in lustrous plates, dissolves sparingly in water, readily in ether and alcohol. The *sodium*, *potassium*, *calcium*, and *barium salts* form crystalline precipitates.

Dimethylnaphthylamine is readily attacked by nitric acid, yielding two nitro-compounds melting respectively at 87—88° and 126—128°.

Tetramethyldiamidodinaphthylphenylmethane, $CHPh(C_{10}H_6{\cdot}NMe_2)_2$, is obtained by heating dimethylnaphthylamine (2 mols.), benzaldehyde (1 mol.), and zinc chloride at 110—120°, dissolving the product in the smallest possible amount of benzene, and adding ether. It separates in lustrous crystals, melts at 188—189°, dissolves sparingly in alcohol and ether, readily in glacial acetic acid, benzene, carbon bisulphide, and in dilute mineral acids. The *platinochloride* is sparingly soluble.

Hexamethyltriamidodinaphthylphenylmethane,

$$NMe_2{\cdot}C_6H_4{\cdot}CH(C_{10}H_6{\cdot}NMe_2)_2,$$

prepared by the action of dimethylparamidobenzaldehyde on dimethylnaphthylamine, forms white needles melting at 178—179°.

Diethyl-α-naphthylamine is readily obtained by heating naphthylamine with aqueous soda and ethyl bromide or iodide at 110—120°, and is purified in a manner similar to dimethylnaphthylamine. It forms a clear oil which gradually becomes brown, and boils at

283—285° (uncorr.). Sp. gr. = 1·005. The *sulphate* crystallises in thick prisms readily soluble in water. The *carboxylic acid*, prepared by the action of carbonyl chloride on the base, forms white plates melting at 166°.

When naphthylamine is heated with ethyl bromide (1·5 part) and alcohol at 120° (Smith, Trans., 1882, 180), a product consisting essentially of monethylnaphthylamine is formed. N. H. M.

α-Naphtholbidiazobenzene and α-Naphthylaminebidiazobenzene. By C. Krohn (*Ber.*, **21**, 3240—3242).—*α-Naphtholbidiazobenzene*, $OH \cdot C_{10}H_5(N_2 \cdot Ph)_2$, $[OH : N_2Ph : N_2Ph = 1 : 2 : 4]$, is readily obtained by adding a solution of diazobenzene chloride (2 mols.) to a slightly alkaline solution of α-naphthol (1 mol.). After 12 hours, the compound separates as a brown powder, and is extracted with boiling, dilute alkali. It is purified by crystallisation from aniline, and will then crystallise well from any solvent. It melts at 183°, and dissolves very readily in chloroform, readily in ether, benzene, and in boiling aniline, sparingly in light petroleum, alcohol, and glacial acetic acid; the solution in strong sulphuric acid is dark-green. When reduced with tin and hydrochloric acid, aniline and diamido-α-naphthol are formed.

α-Naphthylaminebidiazobenzene, $[NH_2 : N_2Ph : N_2Ph = 1 : 2 : 4]$, is prepared by adding a strong aqueous solution of diazobenzene chloride (1 mol.) to an alcoholic solution of naphthylazobenzene (1 mol.) containing sodium acetate; in 12 hours the reaction is finished. It crystallises from aniline in red needles, melts at 189°, and dissolves readily in chloroform, sparingly in most other solvents. The *acetyl-derivative* is yellow, and melts at 265°; the solution in sulphuric acid is brown. When α-naphthylaminebidiazobenzene is reduced with tin and hydrochloric acid, aniline and a triamidonaphthalene are formed; the latter reacts with phenanthraquinone in presence of glacial acetic acid, yielding an azine which dissolves in strong sulphuric acid, forming a green solution. The azo-group is, therefore, in the ortho-position to the amido-group. N. H. M.

Naphthoic Acids. By A. G. Ekstrand (*J. pr. Chem.* [2], **38**, 241—285; compare this vol., p. 52).—The *acetyl*-derivative of amido-α-naphthoic acid (m. p. 211°) forms microscopic needles, melting above 280°; the *calcium* salt crystallises with 3 mols. H_2O in very soluble, violet needles; the *hydrochloride* forms anhydrous, violet needles, soluble in warm water and alcohol, melting above 290°; the *sulphate* and *nitrate* are also described. When the acetyl-derivative is treated with nitric acid (sp. gr. 1·42), *nitracetylamido-α-naphthoic acid* is produced; it melts at 259°, and is easily soluble in alcohol.

When chlorine is passed through a glacial acetic solution of the same amido-α-naphthoic acid containing some iodine, a mixture of ammonium chloride and *dichloronaphthaquinonecarboxylic acid*, $C_{10}H_3O_2Cl_2 \cdot COOH$, is obtained. This acid crystallises in violet needles melting at 255°; when treated with ammonia it is converted into red needles of a *diammonium* salt, $ONH_4 \cdot C_{10}H_3O_2Cl \cdot COONH_4$, of *chlorhydroxynaphthaquinonecarboxylic acid.* From this the acid is obtained by heating with sodium hydroxide solution until all ammonia is expelled, and then adding hydrochloric acid; it crystallises in orange-yellow, rhombic tables melting at 246°; the *acid ammonium* salt is obtained by the action of mineral acids on the diammonium salt.

Chloronitro-α-naphthoic acid, obtained from chlor-α-naphthoic acid (1 : 1′), crystallises in broad prisms melting at 227°; its *ethyl* salt melts at 84°. By reduction, this acid yields *chloramido-α-naphthoic acid*, which crystallises in needles, beginning to melt at 210°, but not fully melted until 285°; its *hydrochloride* is described.

Dichloronitro-α-naphthoic acid is obtained from dichloro-α-naphthoic acid, (COOH : Cl : Cl = 1 : 1′ : 4′), and melts at 165°; it has a very bitter taste.

The *sodium* salt of dinitro-α-naphthoic acid, of melting point 265° (Abstr., 1884, 1361), crystallises with 6 mols. H_2O, and the *barium* salt with 2½ mols. H_2O; the calcium salt is soluble in 138 parts of water at the ordinary temperature. The compound formed when this acid is reduced with hydrogen sulphide in an ammoniacal solution (Abstr., 1886, 949; 1887, 373) contains sulphur as part of the molecule; it would thus appear to be a *sulphide* of *diazinenaphthoic acid*, $S\left[<\genfrac{}{}{0pt}{}{N}{N}>C_{10}H_5\cdot COOH\right]_3$. When the dinitro-acid is reduced with tin and hydrochloric acid, diamidonaphthalene is formed, and at the same time, if the acid is first dissolved in glacial acetic acid, a black powder which appears to be *di-imido-α-naphthoic acid*, $COOH\cdot C_{10}H_5<\genfrac{}{}{0pt}{}{NH}{NH}>$.

The *ethyl* salt of trinitro-α-naphthoic acid (m. p. 283°) crystallises from alcohol in small brown prisms, which melt at 131°; the *calcium* salt crystallises in brown laminæ or needles, with 5 mols. H_2O.

When nitro-α-naphthamide (Abstr., 1886, 948) is reduced with tin and hydrochloric acid, *chloronaphthostyril* is produced; it crystallises in green or yellowish-green needles, which melt at 265° and sublime.

Chloronaphtholactone, $C_{10}H_5ClOCO$ (compare Abstr., 1886, 716), is formed when chlorine is passed through a carbon bisulphide solution of naphtholactone containing some iodine; it melts at 184—185°; when it is dissolved in weak soda solution and hydrochloric acid added, slender needles melting at 190—191° are obtained; these are *chlorhydroxy-α-naphthoic acid.* The *calcium* salt is anhydrous. If the naphtholactone is dissolved in nitric acid (sp. gr. 1·42) and some fuming acid added, *nitronaphtholactone* is formed; it crystallises from glacial acetic acid in slender, yellow needles, melting at 242°, and sparingly soluble in alcohol; by treating it like the chloronaphtholactone, a *nitrohydroxynaphthoic acid* is obtained in rhombic tables, melting at 242°; its *calcium* salt contains 5½ mols. H_2O.

A. G. B.

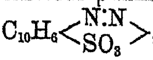
Action of Sulphuric Acid on α-Nitronaphthalene. By W. Palmaer (*Ber.*, **21**, 3260—3264).—Nitronaphthalene is heated on a water-bath with ordinary sulphuric acid (2 parts) and fuming acid (1 part); after 10 hours, the product is poured into water, when the α-sulphonic acid separates. The filtrate is neutralised with chalk and evaporated down; on cooling, the calcium salts of the α- and β-acids separate. The mother-liquor from the calcium salts is treated with potassium carbonate, and the potassium salts converted into chlorides. On crystallising from various solvents, two *chlorides*, $NO_2{\cdot}C_{10}H_6{\cdot}SO_2Cl$, melting respectively at 167° and 126°, were separated. The chloride of higher melting point forms slender, yellowish needles, sparingly soluble in glacial acetic acid; when heated with water in closed tubes, the *acid* is obtained in readily soluble needles. The *ethyl salt*, $NO_2{\cdot}C_{10}H_6{\cdot}SO_3Et$, forms thin, yellow needles, melting at 106—107°. The *amide*, $NO_2{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH_2$, crystallises in small, yellowish-white needles, melting at 223°. When the chloride is distilled with phosphorus pentachloride, dichloronaphthalene melting at 61° is formed. The chloride is, therefore, a derivative of the δ-acid (α-nitro-β-sulphonic acid). The *potassium salt*, $NO_2{\cdot}C_{10}H_6{\cdot}SO_3K + \frac{1}{2}H_2O$, forms very readily soluble, yellow needles; the *sodium salt* crystallises in spherical aggregates of needles; the *silver salt* crystallises in readily soluble, well-formed needles; the barium salt (with $3\frac{1}{2}$ mols. H_2O) forms groups of needles; the anhydrous barium salt dissolves in 9·1 parts of boiling water, and in 377 parts of water at 17°. The *calcium salt* forms long, soft needles, very soluble; the *lead* (with 3 mols. H_2O), *magnesium* (with 9 mols. H_2O), *manganese* (with 10 mols. H_2O), *copper* (with 8 mols. H_2O), and *zinc* (with 10 mols. H_2O) *salts* were also prepared.

The sulphochloride, melting at 126°, forms monoclinic crystals identical with the chloride of β-nitronaphthalenesulphonic acid; $a : b : c = 0{\cdot}9956 : 1 : 0{\cdot}8308$; $\beta = 81° 28'$. N. H. M.

γ-Amidonaphthalenesulphonic Acid. By P. T. CLEVE (*Ber.*, **21**, 3271—3276). *Potassium γ-amidonaphthalenesulphonate*,

$$NH_2{\cdot}C_{10}H_6{\cdot}SO_3K,$$

and the *ammonium salt* are very readily soluble; the *sodium salt* forms readily soluble scales; the *silver salt*, with 1 mol. H_2O, separates in white microscopic needles; the *calcium* and *barium* (with 1 mol. H_2O) *salts* are readily soluble, and crystallise respectively in needles and thin plates; the *lead salt* forms very lustrous prisms.



γ-Diazonaphthalenesulphonic acid, $C_{10}H_6<^{N:N}_{SO_3}>$, crystallises in rather large, yellow crystals.

γ-Amidonaphthalenesulphonamide, $NH_2{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH_2 + H_2O$, prepared by reducing the nitrosulphonamide with hydriodic acid, crystallises in small groups of lustrous needles, melts at 131°, and dissolves readily in dilute hydrochloric acid. The *hydrochloride* forms sparingly soluble, yellow prisms. The *acetyl-derivative*,

$$NH_2{\cdot}SO_2{\cdot}C_{10}H_6{\cdot}NHAc,$$

crystallises from boiling water in tufts of needles, which melt at 220—221°. The *carbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}SO_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, is formed by the action of potassium cyanide on the hydrochloride of the amide. It is amorphous, melts at 273°, is readily soluble in aqueous soda, almost insoluble in water.

γ-Chloronaphthalene sulphochloride, $C_{10}H_6Cl·SO_2Cl$, is prepared by heating the diazosulphonic acid with hydrochloric acid, neutralising the product with potassium carbonate, and treating the potassium salt with phosphorus pentachloride. It is crystallised from light petroleum. It melts at 106°. *Potassium chloronaphthalenesulphonate* crystallises in thin, lustrous scales, rather soluble in boiling water; the *silver salt* forms small, stellate groups of needles; the *barium salt*, with 3 mols. H_2O, forms very sparingly soluble, microscopic needles. The *ethyl salt* crystallises from alcohol in long needles melting at 76—79°. The *amide* forms small, triangular scales, melts at 168°, and is very sparingly soluble in water. N. H. M.

δ-Amidonaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **21**, 3264—3267).—*Potassium δ-amidonaphthalenesulphonate*,

$$NH_2·C_{10}H_6·SO_3K,$$

forms very soluble, thin scales; the *sodium salt* (with ½ mol. H_2O) forms readily soluble, thin needles; the *ammonium salt* crystallises in very soluble, thin plates; the *calcium salt* (with 2 mols. H_2O) is a readily soluble powder and becomes quickly coloured when exposed to air; the *barium salt* crystallises in rather sparingly soluble, flat needles. The *zinc salt* (with 4 mols. H_2O) forms lustrous, yellow, rather sparingly soluble, well-formed needles; the *magnesium*, *lead*, and *silver salts* are also described. The *diazo-acid*, $C_{10}H_6N_2SO_3$, prepared by the action of nitrogen trioxide on the anhydrous acid suspended in absolute alcohol, is a powder. When aqueous alcohol is used, an intensely violet dye of the formula

$$SO_3H·C_{10}H_6·N_2·C_{10}H_5(NH_2)·SO_3H + 2\tfrac{1}{2}H_2O$$

is obtained; this is soluble in water and becomes brown when treated with alkali. The *sulphonamide*, $NH_2·C_{10}H_6·SO_2·NH_2$, is prepared by boiling the nitrosulphonamide dissolved in glacial acetic acid with hydriodic acid; it crystallises in slender, yellowish needles, and melts at 181°. The *hydrochloride*, $NH_2·SO_2·C_{10}H_6·NH_2,HCl + H_2O$, forms slender needles; the hydriodide forms lustrous, yellowish needles soluble in water and alcohol; the *acetyl-derivative*,

$$NHAc·C_{10}H_6·SO_2·NH_2,$$

crystallises from boiling water in slender, white needles melting at 213°. The *carbamide*, $NH_2·CO·NH·C_{10}H_6·SO_2·NH·CO·NH_2$, is prepared by the action of potassium cyanate on the sulphate of the amide; it is an amorphous powder, melts at 225°, and dissolves very sparingly in water, alcohol, glacial acetic acid, &c., readily in aqueous soda.

Amidothionaphthol, $2C_{10}H_6·NH_2·SH + EtOH$, is obtained by heating the amide with hydriodic acid and phosphorus; the thin, lustrous plates of amidothionaphthol hydriodide are treated with ammonia and the oil dissolved in alcohol. It separates in sparingly soluble needles melting at 127°. N. H. M.

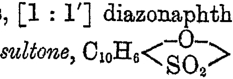
Constitution of Isomeric Naphthalene-derivatives. Part I. αα-Disubstituted Compounds. By H. ERDMANN (*Annalen*, **247**, 306—366).—The naphthylaminesulphonic acids yield α- or β-naphthylamine on the elimination of the sulphonic groups, and α- or β-naphthalenesulphonic acids on the elimination of the amide-groups. The disubstitution products of naphthalene are divided into four classes for the purpose of classification: namely, 3-αα-naphthylaminesulphonic acids; 3-ββ-; 4-α-β-; and 4-β-α-naphthylaminesulphonic acids.

In the preparation of αα-nitronaphthalenesulphonic acid [1 : 4′] from α-nitronaphthalene by Cleve's process, the more soluble isomeride [1 : 1′] is obtained as a bye-product.

The properties of [1 : 4] αα-naphthylaminesulphonic acid have been described by Piria (as *naphthionic acid*) (*Annalen*, **78**, 31), and by Witt (Abstr., 1886, 364). The author has previously shown (Abstr., 1888, 290) that the acid which Witt (Abstr., 1886, 554) obtained by the action of fuming sulphuric acid on α-naphthylamine-hydrochloride is the [1 : 4′] naphthylaminesulphonic acid. The [1 : 1′] acid is obtained from Schöllkopf's patent naphthylaminesulphonic acid S, which consists chiefly of the sparingly soluble sodium salt of this acid. The pure acid forms white needles. 238 parts of boiling water or 4800 parts of water at 21° dissolve 1 part by weight of the acid. The cold, aqueous solution produces a violet coloration in solutions of auric or ferric chloride. The sodium salt crystallises in compact tables or plates, and the potassium salt crystallises in plates. One litre of water dissolves 26·7 grams of the sodium salt at 100° and 11·3 at 24°; also 149 grams of the potassium salt at 100° and 35·6 at 19°. The lead salt crystallises in plates and the silver salt in feathery crystals. Benzaldehyde unites with the sodium salts of the αα-naphthylaminesulphonic acids, forming sodium benzalnaphthylaminesulphonate. The sodium salt of the [1 : 4] acid crystallises with 1 mol. H_2O in golden plates, the [1 : 4′] salt is white, contains 2 mols. H_2O, and is distinguished from the preceding salt by its ready solubility in water. An analogous [1 : 1′] compound is not formed.

Dilute sulphuric acid at 180° converts each of the three isomeric αα-naphthylaminesulphonic acids into α-naphthylamine. In preparing the diazo-compounds, the sulphonic acids must be in a finely divided state, the solutions must be cold and strongly acid, and during the operation the nitrous acid must be present in slight excess. The [1 : 4] diazonaphthalenesulphonic acid is yellow, the [1 : 4′] is grey, and the [1 : 1′] forms greenish-yellow prisms. The latter compound is distinguished from the others by melting without detonation. Reduction with tin and hydrochloric acid converts the diazo-compounds into αα-naphthylhydrazinesulphonic acids. The [1 : 4] acid forms white needles, soluble in hot water, but more freely soluble in hot hydrochloric acid. The sodium salt, $C_{10}H_6(N_2H_3)\cdot SO_3Na + 4H_2O$, crystallises in plates. The [1 : 4′] acid forms plates or groups of needles. Its sodium salt crystallises with 3½ mols. H_2O. The [1 : 1′] acid is deposited in slender plates. The potassium and sodium salts are anhydrous. The latter is characterised by its sparing solubility in water. The ammonium salt is freely soluble.

The three isomeric acids yield α-naphthalenesulphonic acid on boiling with an acid solution of cupric chloride.

The 1 : 4- and 1 : 4′-*naphtholsulphonic acids* are prepared by dissolving the corresponding diazonaphthalenesulphonic acids in boiling sulphuric acid diluted with four times its weight of water. The former has been described by Neville and Winther (Trans., 1880, 632). The latter is a deliquescent, crystalline substance, and melts between 110° and 120°. Under similar conditions, [1 : 1′] diazonaphthalenesulphonic acid yields an anhydride, *naphthosultone*,  $C_{10}H_6<\begin{smallmatrix}-O-\\SO_2\end{smallmatrix}>$. The sultones bear the same relation to γ-hydroxysulphonic acids that the lactones do to γ-hydroxycarboxylic acids. Naphthosultone crystallises in prisms, melts at 154° and boils above 360° with partial decomposition. It is soluble in chloroform and in warm benzene. At the ordinary temperature, alkalis do not act on the sultone, but at 130° alcoholic ammonia converts it into the ammonium salt of [1 : 1′] naphtholsulphonic acid, $OH{\cdot}C_{10}H_6{\cdot}SO_3NH_4$. The ammonium salt is freely soluble in water, and the solution gives a precipitate with lead salts, and also on boiling with an excess of sodium hydroxide, the basic sodium salt $C_{10}H_6SO_4Na_2 + 1\frac{1}{2}H_2O$. The free acid crystallises with 1 mol. H_2O, and produces with ferric chloride a deep green coloration changing to red.

The conversion of [1 : 4]- and [1 : 4′]-naphthylaminesulphonic acids into the corresponding dichloronaphthalenes has been previously described by the author (Abstr., 1888, 290), but the [1 : 1′]-diazosulphonic acid, on treatment with phosphorus pentachloride, yields *chloronaphthosultone*, $C_{10}H_5ClSO_3$. This compound forms yellow needles, and melts at 174—175°. It is not attacked by alkaline solutions at the ordinary temperature.

[1 : 4]-Dihydroxynaphthalene is identical with α-naphthahydroquinol; [1 : 4′]-dihydroxynaphthalene has been described by Bernthsen and Semper (Abstr., 1887, 674). The [1 : 1′]-dihydroxynaphthalene is obtained from naphthosultone by fusion with potassium hydroxide. It crystallises in needles or plates and melts at 137—138°, and dissolves freely in ether, benzene, and toluene. The *diacetate*, $C_{10}H_6(OAc)_2$, melts at 147—148°.

Two αα-dinitronaphthalenes are known; [1 : 4′] melts at 218° and [1 : 1′] at 170°.

Aguiar (*Ber.*, 7, 309) has described the preparation and properties of [1 : 4′]- and [1 : 1′]-diamidonaphthalenes from the corresponding dinitronaphthalenes. W. C. W.

The Dextrorotatory Terebenthene. By L. Pesci (*Chem. Centr.*, 1888, 1097—1098, from *Ann. Chim. Farm.*, 7, 353—358).—The terebenthene was obtained from American turpentine by fractionating in a vacuum, and was found to be the principal product; sp. gr. = 0·8641, boiling point 156—157°. Specific rotation $[\alpha]_D$ = + 13·945°. The American turpentine contains also lævorotatory substances.

Nitroterebenthene was prepared by treating the terebenthene with potassium nitrite and dilute sulphuric acid, the green oily product was shaken with ammonia, washed with dilute hydrochloric acid, and distilled twice in a current of steam. It is a yellow liquid, having the odour of peppermint oil. Sp. gr., 1·0499; specific rotation, $[\alpha]_D = +2·984$. By reduction with zinc and acetic acid, the same amidoterebenthene, $C_{10}H_{15}NH_2$, was obtained as the author prepared from the lævorotatory terebenthene. The hydrochlorides of both show the same specific rotation: $[\alpha]_D = -48·508°$ and $-48·629°$.

The *hydrochloride of lævoterebenthene* possesses the specific rotation $[\alpha]_D = -30·687°$, melting point 125°. *Lævoterebenthene hydrobromide:* specific rotation $[\alpha]_D = -27·802°$ and melting point 87°.

Dextroterebenthene hydrochloride and *hydrobromide* are optically inactive. Their melting points are 125° and 91° respectively. These facts go to prove the non-identity of the two terebenthenes.

J. W. L.

Hydroxycamphoronic Acids. By J. Kachler and F. V. Spitzer (*Monatsh.*, **9**, 708—726).—The two isomeric hydroxycamphoronic acids, formed by the action of aqua regia on camphoronic acid, correspond in their crystalline form with the two modifications which Kachler obtained by heating camphoronic acid with bromine and subsequent treatment with water. Further investigations of the compounds obtained by the action of bromine show that they are not chemically identical as previously suggested. In order to isolate the isomerides, the mixture of acids dissolved in a small quantity of warm water is treated with aqueous baryta until the solution gives only a feebly acid reaction. Ammonia is added until the solution is distinctly alkaline, and the mixture shaken for some time, when bibasic barium α-hydroxycamphoronate separates out, the β-salt remaining in solution.

α-Hydroxycamphoronic acid, $C_9H_{14}O_7$, crystallises in monoclinic plates or prisms. It is only slightly soluble in ether, dissolves readily in cold water and alcohol, softens at 100°, and melts at 216·5° (corr.). On long exposure to air, or more quickly over sulphuric acid, the crystals lose water and are converted into the anhydride $C_9H_{12}O_6$, which, on heating, loses more water, forming the anhydride $C_9H_{10}O_5$. This is a crystalline powder, which dissolves readily in alcohol and water, and melts at 135—137°. Both anhydrides are reconverted into the acid by boiling with water. The salts of the α-acid are mostly easily soluble in water. The acid potassium salt, $C_9H_{13}KO_7$, crystallises in stout needles, the dipotassium salt, $C_9H_{12}K_2O_7 + \frac{1}{2}H_2O$, in scales; when heated at 100°, the latter yields the compound $C_9H_{10}K_2O_6$. The calcium salt, $C_9H_{12}CaO_7 + 4H_2O$, crystallises in bundles of needles; the barium salt, $C_9H_{12}BaO_7$, in thin plates only, slightly soluble in water; the silver salt, $C_9H_{12}Ag_2O_7 + H_2O$, forms minute crystals; the copper and lead salts are anhydrous. All the above-mentioned salts in the anhydrous condition lose the elements of a molecule of water when heated. The ethyl compound, $C_9H_{11}EtO_6$, crystallises in rhombic plates melting at 158° (corr.). If heated, it gives the anhydride of α-hydroxycamphoronic acid and alcohol, and on passing ammonia through the ethereal solution, the salt $C_6H_{10}EtO_6·NH_4$, crystallising in needles, melting at 168—170°, is formed.

β-Hydroxycamphoronic acid is not so soluble as its isomeride. When air-dried, it has the formula $C_9H_{14}O_7$, melts at 250·9° (corr.), but loses water on heating, forming an anhydride, and furnishes mono-, di-, and tri-basic salts, of which the tribasic salts of lead and barium are insoluble. The potassium salt, $C_9H_{12}K_2O_7 + \frac{1}{2}H_2O$, is hygroscopic. The barium salt, $C_9H_{12}BaO_7 + 4H_2O$, crystallises in needles. The ethyl-derivative, $C_6H_{10}EtO_6$, forms needles melting at 158·5—159·5° (corr.), and resembles its isomeride, forming with ammonia the compound $C_9H_{10}EtO_6{\cdot}NH_4$, melting at 165°.

The authors find that when camphoronic acid is heated with bromine no bromo-derivative is produced, but the above-mentioned anhydrides which, on treatment with water, yield a mixture of α- and β-hydroxycamphoronic acid. G. T. M.

Syringin. By G. Körner (*Chem. Centr.*, 1888, 1098—1099, from *Rend. R. Inst. Lombardo* [2], **21**, 563—572).—The author finds that syringin, formerly considered as a glucoside, is hydroxymethylconiferin, $C_{17}H_{24}O_7$. He prepares it according to Kromayer's method (*Die Bitterstoffe*, 1861, 56). It crystallises from water in long, slender, white needles, which are only sparingly soluble in cold water, but readily in hot. It contains water of crystallisation, which is given off at 100°. Melting point 191—192°. It does not form insoluble compounds with solutions of metallic salts; it reacts with mineral acids similarly to coniferin. By the action of emulsin, syringin is split up into dextrose and *syringenin*, $OH{\cdot}C_6H_2(OMe_3)_2{\cdot}C_3H_4{\cdot}OH$ (*hydroxymethylconiferyl alcohol*); the latter resembles coniferyl alcohol.

By oxidising syringin with potassium permanganate, *glucosyringic acid*, $C_{15}H_{20}O_{10}$, is formed, crystallising from water in slender, colourless needles with 2 mols. H_2O. It is sparingly soluble in cold water, readily in hot. Melting point about 208°. When crystallised from alcohol, it melts at 214°. Thus prepared it contains no combined water. The lead salt is but little soluble; the salts of potassium and barium crystallise in needles. By heating glucosyringic acid with dilute sulphuric acid, it splits up into dextrose and *syringic acid*, $C_9H_{10}O_5$. This decomposition is also effected by the action of emulsin at 30°.

By the oxidation of syringin with cold, very dilute chromic acid, *glucosyringinaldehyde* is formed; it is soluble in water, but only sparingly in alcohol, and insoluble in ether. It combines with phenylhydrazine, the compound crystallising in needles, and melting at 156°.

The aldoxime is decomposed by emulsin or dilute sulphuric acid into glucose and *syringinaldehyde*, $C_9H_{10}O_4$, which has the smell of vanilla. It reacts readily with phenylhydrazine and hydrogen sulphites, forming soluble compounds. Syringic acid is sparingly soluble in cold water, more readily in hot water, soluble in alcohol. It is monobasic and melts at 202°. The barium salt crystallises with 3 mols. H_2O. The *methyl* salt, $C_9H_9O_5Me + H_2O$, is soluble in hot water, and melts at 83·5°. Syringic acid, when heated with hydrogen iodide a little above 100°, decomposes with liberation of methyl iodide. With sodium methyl oxide and methyl iodide it forms *methyl methylsyringate*, $C_{11}H_{14}O_5$, melting at 82·5°. *Methylsyringic acid*, $C_{10}H_{12}O_5$, melts at 168°, and is somewhat soluble in hot water. Distillation with calcium hydroxide produces trimethylpyrogallol. By heating syringic acid above 225°, dimethylpyrogallol, $OH{\cdot}C_6H_3(OMe)_2$, is formed; with ferric chloride it gives at first a blood-red coloration, which changes into copper-red needles. Cedriret was observed in the solution. Methylsyringic acid was identified as trimethylgallic acid.

J. W. L.

Arganin. By S. Cotton (*J. Pharm.* [5], **18**, 298—302).—This bitter principle is extracted from the kernel of the nut borne by the argan tree, of the order *Sapotaceæ*, growing in Morocco and Madagascar. The almond itself is bitter but contains over 66 per cent. of a sweet, fixed oil, which congeals at 0°, and has a density of 0·914. The bitter principle, insoluble in oil, ether, chloroform, carbon bisulphide, and light petroleum, is easily soluble in water and 90° alcohol; and somewhat less soluble in absolute alcohol. It is extracted by treating the crushed kernels with ether or some other solvent to remove the oil, then extracting with 99° alcohol with the aid of heat. The alcoholic solution is then treated fractionally with ether at intervals, so as to obtain the arganin in crystals. After some days, the liquid is decanted and the crystals are dissolved in boiling absolute alcohol, from which they recrystallise on cooling. Very short, brilliant prisms are thus obtained, which become gummy on the filter from exposure to the moisture of the air.

J. T.

Homopterocarpin and Pterocarpin from Red Sandal Wood. By P. Cazeneuve and L. Hugounenq (*Compt. rend.*, **107**, 737—740).—When homopterocarpin is heated just to the point at which decomposition begins, it yields creosote and a small quantity of catechol, and when distilled with zinc powder, it yields a small quantity of a volatile oil with an odour of coumarin, together with benzene, toluene, methane, ethylene, and carbonic oxide. The principal product of the action of hydrochloric acid on homopterocarpin (Abstr., 1887, 972) is a black, uncrystallisable resin, which dissolves in alkalis and forms fluorescent solutions; the hydrochloric acid retains in solution a small quantity of an amorphous, red colouring matter, which dissolves in alkalis with fluorescence and probably belongs to the fluoresceïn-group. Hydriodic acid produces similar results. When heated in sealed tubes with 10 per cent. sulphuric acid, homopterocarpin undergoes an isomeric change, and is converted into an opaline, yellowish, non-crystallisable resin, similar in appearance to amber, whilst the sulphuric acid remains unaltered. Homopterocarpin is not affected by aqueous potash at 200°, but is attacked by fused potash at 250—300°, and yields a small quantity of a volatile oil with an odour of coumarin, and phloroglucinol, but no acid. Ordinary nitric acid attacks homopterocarpin in the cold, with formation of an amorphous, green, unstable nitroso-derivative, which contains 3·5 per cent. of nitrogen. Fuming nitric acid acts with considerable energy, and on the addition of water an insoluble red resin separates. The aqueous solution when evaporated yields a crystalline product, from which cold water extracts oxalic acid, whilst hot water dissolves a substance which crystallises in yellow needles melting at 162°, and has all the properties of trinitro-orcinol. It yields a barium salt $C_7H_2(NO_2)_3O_2Ba + 3H_2O$, which crystallises in yellow needles, and explodes above 150°. The product of the action of nitric acid also contains a non-crystallisable isomeric trinitro-orcinol. If homopterocarpin is treated with excess of bromine, the compound $C_{24}H_{18}Br_6O_6$ is obtained; it dissolves in benzene and separates in crystalline plates melting at 270°, when the benzene is mixed with an equal volume of ether. The interaction of equal molecular proportions of homopterocarpin and bromine in solution in chloroform yields a mono-derivative, $C_{24}H_{23}BrO_6$, which separates from boiling alcohol in white crystals. Phenylhydrazine and acetic anhydride have no action on homopterocarpin. From these results, it follows that the formula originally ascribed to homopterocarpin must be doubled, and it would seem to be a condensed poly-orcinol, but its constitution is not yet definitely determined.

Pterocarpin yields similar results, but the action of nitric acid is more energetic. It yields a crystalline monobromo-derivative, $C_{20}H_{15}BrO_6$, and hence its true formula is $C_{20}H_{16}O_6$. Pterocarpin is in all probability a lower homologue of homopterocarpin.

C. H. B.

Dipicolylmethane. By A. LADENBURG (*Ber.*, **21**, 3099—3104).—*Dipicolylmethane*, $CH_2(CH{\cdot}C_5NH_4)_2$, is obtained by heating a mixture of picoline (from the mercury salt) with methylal in molecular proportion, in presence of zinc chloride for 10 hours, at 280—290°. The product is treated with dilute hydrochloric acid, heated on a water-bath for some time, made alkaline, and distilled. The residue is extracted repeatedly with ether, and the base extracted from the ethereal solution with dilute hydrochloric acid. The solution is treated with mercuric chloride as long as any resin is precipitated, filtered, freed from mercury by means of hydrogen sulphide, made alkaline with soda, and extracted with ether. The base is distilled under reduced pressure. It is a light-yellow oil, insoluble in water, readily soluble in alcohol and ether, and boils at 319—323° under 760 mm. pressure. Sp. gr. = 1·0281 at 0°. The *hydrochloride* forms deliquescent needles; the *platinochloride*, $C_{13}H_{14}N_2,H_2PtCl_6$, crystallises from water in sparingly soluble, lustrous plates which melt at 215° with decomposition; the *aurochloride*, $(C_{13}H_{14}N_2)_3,H_4Au_3Cl_{13} + 1\frac{1}{2}H_2O$, separates as an oil which solidifies to small needles; the *mercurochloride*,

$$C_{13}H_{14}N_2,H_2Hg_4Cl_{10},$$

crystallises like ammonium chloride, or in large plates, and melts at 161°; the *picrate*, *cadmioiodide*, *periodide*, and *bismuthoiodide* were prepared.

Dipipecolinemethane, $C_{13}H_{26}N_2$, prepared by reducing the above compound with sodium and alcohol, forms a white, crystalline mass, melts at 52—54°, and boils at 195° under 26 mm. pressure. It dissolves readily in benzene and ether, very readily in alcohol, and is rather sparingly soluble in water. It is a strong base, but yields mostly oily salts. The *hydrochloride*, $C_{13}H_{26}N_2,2HCl$, is crystalline. *Tetramethyldipipecolyl methiodide*, $C_{13}H_{24}Me_2N_2,2MeI$, forms white crystals, very readily soluble in water; the *aurochloride*, $C_{13}H_{24}Me_2N_2,H_2Au_2Cl_8$, crystallises in needles melting at 170—171°, with decomposition. The constitution of the base is probably $CH_2(CH_2{\cdot}C_5NMeH_9)_2$.

N. H. M.

The Two Bidesyls. By J. C. GARRET (*Ber.*, 21, 3107—3108).—Both bidesyls (Knoevenagel, Abstr., 1888, 706) yield *tetraphenylpyrroline*, $C_{28}H_{21}N$, when heated with alcoholic ammonia at 150°. This crystallises in large needles, melts at 211—212°, and is almost insoluble in alcohol. On one occasion, the preparation from isobidesyl melted at 234—235°, but was otherwise identical with the other preparations.

N. H. M.

Methylstilbazole and its Reduction-products. By F. BACHÉR (*Ber.*, 21, 3071—3082).—*Methylstilbazole*, $C_{14}H_{13}N$, is formed when α-γ-lutidine is heated at 215° with benzaldehyde (1 mol.) and anhydrous zinc chloride. The product is mixed with alcohol, acidified with hydrochloric acid, distilled with steam to free it from benzaldehyde and hydrocarbons, and the residual oily liquid separated. After adding excess of soda, the mixture is distilled with superheated steam; the unchanged lutidine which passes over first is collected separately, and the new base, which is very slightly volatile, is extracted from the latter portions of the distillate with ether, the solution dried over potash, evaporated, and the base distilled. The yield is about 15·4 per cent. of the theoretical quantity. It is a yellow, viscid, strongly refractive oil, boils at 321—326° with slight decomposition, and is readily soluble in alcohol, ether, chloroform, and carbon bisulphide, but insoluble in water.

The *hydrochloride* and the *hydrobromide* cannot be obtained in crystals, but the *hydriodide*, prepared by dissolving the base in fuming hydriodic acid, crystallises from hot alcohol in microscopic, yellow needles melting at 210—211°. The *periodide* is crystalline, and readily soluble in alcohol, but insoluble in water. The *picrate*, $C_{14}H_{13}N,C_6H_3N_3O_7$, crystallises from hot alcoholic hydrochloric acid in microscopic, yellow needles, melts at 192—193° with previous softening, and is very sparingly soluble in hot dilute hydrochloric acid. The *mercurochloride*, $C_{14}H_{13}N,HHgCl_3$, crystallises in needles, has no well-defined melting point, and is soluble in dilute hydrochloric acid. The *platinochloride*, $C_{14}H_{13}N,H_2PtCl_6$, crystallises in small, yellow needles with 1 mol. H_2O, melts at 183°, decomposes at 188°, and is soluble in hot dilute alcohol, but very sparingly soluble in hot hydrochloric acid. The *aurochloride*, $C_{14}H_{13}N,HAuCl_4$, prepared by precipitating a boiling solution of the hydrochloride, crystallises in golden needles, melts at 141—142°, and is sparingly soluble in boiling water. Potassium bismuth iodide, potassium cadmium iodide, and stannous chloride produce precipitates in a hydrochloric acid solution of the base. The *bromide*, $C_{14}H_{13}Br_2N$, prepared by treating the base with bromine (1 mol.) in carbon bisulphide solution, separates from hot alcohol in small, nodular crystals, and melts at 139—140°.

Dihydromethylstilbazole, $C_{13}H_{15}N$, is prepared by heating methylstilbazole (1 part) with fuming hydriodic acid (10 parts) at 160°, treating the resulting periodide with sulphurous anhydride, decomposing the iodide with soda, and distilling the base with steam. It is a colourless oil boiling at 290—295°. The *picrate*, $C_{14}H_{15}N,C_6H_3N_3O_7$, crystallises in small, citron-yellow needles, melts at 154—156°, and is readily soluble in hot alcohol, but only sparingly in ether. The *platinochloride*, $C_{14}H_{15}N,H_2PtCl_6$, is crystalline, melts at 168° with decomposition, and is very sparingly soluble in water, but more readily in dilute alcohol. The *mercurochloride*, $C_{14}H_{15}N,HHgCl_3 + H_2O$, crystallises from hot, dilute hydrochloric acid, in which it is readily soluble, in large needles, and melts at 93—95°. The remaining salts cannot be obtained in a crystalline condition.

Methylstilbazoline, $C_{14}H_{21}N$, is prepared by reducing a boiling alcoholic solution of methylstilbazole with sodium and distilling the product with steam; it is a colourless oil, boils at 286—291°, and becomes yellow on keeping. It is readily soluble in alcohol and ether, but sparingly in water, to which it imparts an alkaline reaction. It yields an oily nitrosamine, and all the salts examined were also oily compounds.

Methylpyridinecarboxylic acid, $C_5NH_3Me{\cdot}COOH$, is obtained in small quantity when α-γ-lutidine is oxidised with the calculated quantity of a 1½ per cent. solution of potassium permanganate, but the principal product is lutidinic acid. Methylpyridinecarboxylic acid crystallises from hot alcohol, in which it is only moderately soluble, in small plates, decomposes at about 260° and is very readily soluble in water. It gives no reaction with ferrous salts, and yields picoline when heated with lime.

When α-γ-lutidine is heated at about 225° with benzaldehyde (2 mols.) and anhydrous zinc chloride, an oily, seemingly neutral compound is obtained. F. S. K.

β-Ethyl-α-stilbazole and its Derivatives. By G. PLATH (*Ber.*, **21**, 3086—3099).—*β-Ethyl-α-stilbazole*, $C_5NH_3Et{\cdot}CH{:}CHPh$ [= 3 : 6], is formed when collidine (10 grams), prepared from paraldehyde and aldehyde-ammonia (compare Dürkopf, Abstr., 1887, 499), is heated at 220—222° with benzaldehyde (9 grams) and zinc chloride. The product is acidified and distilled with superheated steam to free it from benzaldehyde and hydrocarbons. Excess of alkali is then added, the unchanged collidine distilled with steam, and, as soon as the distillate commences to become turbid, the steam is superheated, and the distillate containing the new base, which is only very slightly volatile, is collected separately. The yield is about 37 per cent. of the theoretical quantity. It crystallises from dilute alcohol in colourless plates, melts at 58·5°, boils at 344°, and is readily soluble in alcohol, ether, benzene, acetone, and chloroform, but insoluble in water. The *hydrochloride*, $C_{15}H_{15}N,HCl$, separates from hot benzene in an oily condition, but solidifies on cooling; it crystallises in needles and melts at 193°. The *platinochloride*, $(C_{15}H_{15}N)_2,H_2PtCl_6 + 2H_2O$, crystallises in needles, melts at 188° with decomposition, and is soluble in dilute hydrochloric acid, but insoluble in cold water. The *aurochloride*, $C_{15}H_{15}N,HAuCl_4$, crystallises in long needles, melts at 168°, and is insoluble in water. The *stannochloride*, $C_{15}H_{15}N,HSnCl_3 + 3H_2O$, crystallises from hot dilute hydrochloric acid in white needles, melting at 245·5—246°. The *mecrurochloride*, $C_{15}H_{15}N,HAgCl_3$, crystallises from hot dilute hydrochloric acid in long needles melting at 196°. The *picrate*, $C_{15}H_{15}N,C_6H_3N_3O_7$, crystallises from alcohol or hot water in long, yellow needles melting at 203°. An aqueous solution of the hydrochloride gives precipitates with ammonium molybdate, potassium dichromate, and potassium cadmium iodide. The *periodide* is crystalline but unstable. The *bromide*, $C_{15}H_{15}Br_2N$, prepared by treating the base with bromine (1 mol.) in carbon bisulphide solution, crystallises from alcohol in small needles, melts at 127·5—128°, and is very readily soluble in chloroform, carbon bisulphide, benzene, alcohol, and ether, but insoluble in water.

Dihydroethylstilbazole, $C_5NH_3Et\cdot CH_2\cdot CH_2Ph$ [= 3 : 6], is obtained when ethylstilbazole is heated at 160—165° with concentrated hydriodic acid. The product is treated with sulphurous anhydride, the resulting iodide dissolved in water, and the solution shaken with ether; excess of soda is then added, the base extracted with ether and distilled. It is a colourless oil, boils at 316·33° (corr.), and is readily soluble in alcohol and ether, but insoluble in water. The *aurochloride*, $C_{15}H_{17}N,HAuCl_4 + H_2O$, and the *hydrochloride*, are with difficulty obtained in a crystalline state. The *platinochloride*, $(C_{15}H_{17}N)_2,H_2PtCl_6$, crystallises from dilute hydrochloric acid in long needles melting at 168°. The *mercurochloride*, $C_{15}H_{17}N,HHgCl_3$, crystallises from very dilute hydrochloric acid in long needles, and melts at 136·5°. The *picrate* is sparingly soluble in water, from which it crystallises in yellow needles.

Octohydroethylstilbazole, $C_5NH_7Et\cdot CH_2\cdot CH_2Ph$, prepared by treating a boiling alcoholic solution of ethylstilbazole with sodium and purifying the product by means of the nitroso-derivative, is a colourless oil boiling at 303° (uncorr.). It has a strong, piperidine-like odour, an alkaline reaction, and is volatile with steam. It is soluble in chloroform, benzene, ether, and alcohol, but only sparingly in water. No crystalline salts were obtained. F. S. K.

Paraxyloquinolinesulphonic Acids. By E. NÖLTING and J. FRÜHLING (*Ber.*, **21**, 3156—3158).—*Xyloquinolinesulphonic acid*, [$Me_2 : SO_3H$ = 1 : 4 : 2] (compare Nölting and Kohn, Abstr., 1886, 355), crystallises in prisms, and is very readily soluble in hot water and dilute acetic acid, but only sparingly in cold water. The *barium* salt, $(C_{11}NH_{10}\cdot SO_3)_2Ba + H_2O$, crystallises in needles, loses its water at 150°, and is readily soluble in hot water. The *potassium* salt crystallises with 1 mol. H_2O, and is readily soluble.

Xyloquinolinesulphonic acid, [$Me_2 : SO_3H$ = 1 : 4 : 3], can be prepared from paraxylidineparasulphonic acid by Skraup's reaction, or by heating paraxyloquinoline with fuming sulphuric acid for 36 hours. It resembles the preceding compound, but is more sparingly soluble. The *barium* salt crystallises in plates with 1 or 2 mols. H_2O. The *potassium* salt crystallises in anhydrous needles or plates.

Paraxyloquinoline is obtained when either of the above acids or any of their salts is distilled with ammonium chloride, but it is more easily prepared from paraxylidine. F. S. K.

Isoquinoline. By G. GOLDSCHMIEDT (*Monatsh.*, **9**, 675—684).—The author has previously shown (Abstr., 1888, 302) that papaverine and its compounds with methyl iodide and ethyl iodide yield imides of hemipinic acid when oxidised with permanganate. This property of forming imides on oxidation with permanganate appears to be common to all isoquinoline-derivatives, the base itself giving phthalimide.

Isoquinoline ethobromide, on oxidation, appears to give ethylphthalimide, but the quantity obtained was insufficient for analysis.

Isoquinoline benzyl chloride is formed on mixing its constituents in molecular proportion. It crystallises, although not easily, in prisms, dissolves readily in water and alcohol, but is only slightly soluble in ether and benzene. When oxidised with permanganate, it gives benzylphthalimide melting at 115—116°.

Isoquinoline phenacyl bromide is most conveniently prepared by mixing molecular proportions of its constituents dissolved in benzene. It crystallises from alcohol in prisms, which melt at 205° to a golden-red liquid, and furnishes a nitro-compound which in its toxicological action resembles the corresponding quinoline-derivative. On oxidation with permanganate, a nearly pure phenacylphthalimide, melting at 156—158°, was formed. G. T. M.

Creatinines. By G. S. JOHNSON (*Proc. Roy. Soc.*, **43**, 493—534).—Normal urine when boiled with picric acid in alkaline solution causes a reduction to picramate. About one-fourth of the cupric oxide reducing power of normal urine is due to uric acid, whilst the remaining three-fourths has been variously accounted for. The author finds that it is due to a creatinine which can be best precipitated by adding sodium acetate and mercuric chloride to normal urine. A flocculent precipitate is first produced, which is succeeded by one which is apparently crystalline, but which under the microscope is found to consist of globules. It has a constitution $4(C_4H_5HgN_3O,HCl),3HgCl_2 + 2H_2O$. The hydrochloride of the base, $C_4H_7N_3O,HCl$, is prepared by decomposing the mercury salt with hydrogen sulphide. It is soluble in water and alcohol. No precipitate is produced with mercuric chloride until sodium acetate has been added. With platinum chloride in alcoholic solution it gives an anhydrous salt, $(C_4H_7N_3O)_2,H_2PtCl_6$; in aqueous solution a salt, $(C_4H_7N_3O)_2,H_2PtCl_6 + 2H_2O$, is formed. The free base is obtained by treating the hydrochloride with lead hydroxide; it can be obtained in three forms, according to the temperature at which the solution is evaporated. If the crystals are dissolved in a small quantity of cold water and evaporated in a vacuum, efflorescent creatinine is obtained in square prisms, which acquire a porcelain-like appearance as the water of crystallisation evaporates. But if the evaporation is conducted at 60°, anhydrous crystals of tabular β-creatinine of urine are obtained, which when dissolved and again evaporated in the cold give efflorescent creatinine. Finally if effloresced creatinine is dissolved at 100°, tabular α-creatinine of urine is obtained, and this when dissolved and evaporated in the cold recrystallises unchanged; 2 mols of creatinine of urine are equivalent in reducing power to 1 mol. of glucose, whilst

3 mols. of flesh creatinine are required to effect the same amount of reduction. The efflorescent creatinine has the same solubility in water as the tabular α-salt. Urine creatinine differs from flesh creatinine in its power of reduction, in the composition of its platinochloride, and in its solubility in water and alcohol. Boiled with water, the creatinine is converted into urinary creatine, $C_4H_9N_3O + H_2O$. It can be converted by Liebig's process into a creatinine hydrochloride, which is identical with that obtained from flesh creatine by the same process. From this hydrochloride four different creatinines are obtained, which are not identical with the above creatinines directly prepared. Crystallographic measurements of the natural creatinines are given. The creatinines from urinary creatine have less reducing powers than the natural creatinines, but greater than that of creatinine from flesh creatine.

Measurements by Hartley of the absorption-spectra of creatinine from flesh creatine (Liebig's process), and of the new base from urine, are given. The spectra are similar, the bands being caused by condensation of numerous oxygen- and nitrogen-atoms, as in uric acid. The actinic absorption is greater for the urine creatinine than for creatinine from flesh. H. K. T.

Bases formed by the Action of Potash on Additive Products of Papaverine. By A. STRANSKY (*Monatsh.*, 9, 751—761; compare Claus and Ritzfeld, Abstr., 1886, 996).—On boiling papaverine ethobromide with aqueous potash for several hours, a brown, resinous substance is formed. It may be crystallised from water and alcohol, and forms prismatic plates, which have the formula $O(C_{20}H_{21}NO_4Et)_2$, and melt at 72°. From this oxide, the following compounds may be obtained:—The chloride, $C_{20}H_{21}NO_4EtCl$, which crystallises from alcohol in rhombic needles melting at 80°; the platinochloride, $(C_{20}H_{21}NO_4EtCl)_2,PtCl_4$; the picrate, crystallising in light yellow plates; and the chromate, $(C_{20}H_{21}NO_4Et)_2Cr_2O_7$, crystallising in yellow needles or plates and melting at 78°.

Papaverine benzyl chloride under the same conditions gives the oxide, $(C_{20}H_{21}NO_4C_7H_7)_2O$, which crystallises in needles melting at 165°. The chromate, $(C_{20}H_{21}NO_4C_7H_7)_2Cr_2O_7$, forms yellow plates, which melt with decomposition at 85°, and the picrate,

$$(C_{20}H_{21}NO_4C_7H_7)C_6H_2N_3O_7,$$

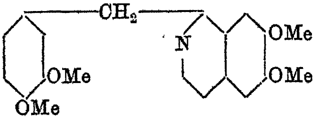
crystallises in plates melting at 185°.

Pavaverine methiodide (30 grams), potash (60 grams), and water (300 grams) when boiled together for 20 minutes give a product crystallising in greenish-yellow needles melting at 215°, efflorescing on exposure to air, and giving the hydroxide $C_{20}H_{21}NO_4Me{\cdot}OH$ when heated at 100°. The corresponding picrate crystallises in plates melting at 205°, and the chromate in small needles melting at 85°. G. T. M.

Papaverine-derivatives. By G. GOLDSCHMIEDT and C. OSTERSETZER (*Monatsh.*, 9, 762—777; compare Abstr., 1886, 83, 478; 1887, 163; 1888, 302, 1116, 1118).—The authors find that the two acids of the formula $C_{10}H_{10}O_6$, obtained by the oxidation of narcotine and papaverine respectively, are not identical, as was previously supposed. The acid from narcotine (hemipinic acid) forms crystals belonging to the monoclinic system, commences to fuse in open tubes at 160—161°, in closed tubes at 156—158°, and gives an orange-red precipitate with ferric chloride, but no precipitate with silver nitrate. The corresponding anhydride melts at 166—167°, the ethylimide at 96°. The acid from papaverine (*metahemipinic acid*) crystallises in the rhombic system, commences to fuse in open tubes at 174—175°, in closed tubes at 172—173°, gives a deep orange-red precipitate with ferric chloride, and a crystalline precipitate (needles) with silver nitrate. The corresponding *anhydride* melts at 175°, the *ethylimide* at 230°.

G. T. M.

Constitution of Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, 9, 778—781; compare preceding Abstracts).—Metahemipinic acid obtained by the oxidation of papaverine is dimethoxy-orthophthalic acid, $C_6H_2(OMe)_2(COOH)_2$ $[(OMe)_2 : (COOH)_2 = 1 : 2 : 4 : 5]$, and differs from hemipinic acid by giving protocatechuic acid $[COOH : (OH)_2 = 1 : 3 : 4]$ on fusion with potash. The constitution of papaverine must therefore be represented by the formula—



G. T. M.

Strychnine. By W. F. LOEBISCH and H. MALFATTI (*Monatsh.*, 9, 626—633; compare Abstr., 1887, 282).—Stoehr, on distilling strychnine with quicklime, obtained a mixture of scatole, and β-methylpyridine. The authors find that when the alkaloïd is distilled with soda-lime, in addition to the above-mentioned compounds, carbazole is formed, in quantity equal to 0·5 per cent. of the strychnine used.

G. T. M.

Relations between Atropine and Hyoscyamine. By A. LADENBURG (*Ber.*, 21, 3065—3070).—The author is of the opinion that atropine is an inactive base, and that it stands in the same relation to hyoscyamine as racemic acid to lævotartaric acid; moreover, that the supposed conversion of atropine into hyoscyamine, although possible, has not hitherto been accomplished, and that all observations to the contrary result from the employment of impure atropine. (Compare Will and Bredig, Abstr., 1888, 1316.) This view is supported by the following experiments:—20 grams of atropine aurochloride, prepared from "pure" atropine, was recrystallised 14 times, and yielded 1 gram of hyoscyamine aurochloride. Another sample of atropine aurochloride, prepared from the purest commercial atropine, which had been further purified by recrystallising many times, and then melted at 114°, was recrystallised 14 times. 1 gram of atropine aurochloride was obtained; it melted at about 140°, and an 18 per cent. solution of the free base prepared from this sample of salt was optically inactive.

Atropine cadmioiodide crystallises from alcohol in needles, and is almost insoluble in water. F. S. K.

Constitution of Berberine. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, **7**, 206—209).—The view is expressed that berberine is a derivative of isoquinoline, and the authors are engaged on experiments with the object of proving this.

Commercial Preparation and Partial Synthesis of Cocaïne. By C. LIEBERMANN and F. GIESEL (*Ber.*, **21**, 3196—3202).—Most of the amorphous alkaloïds, obtained in the preparation of cocaïne, yield ecgonine when boiled for about an hour with hydrochloric acid (compare Liebermann, Abstr., 1888, 1210). The ecgonine can be isolated by evaporating the filtered solution to dryness, boiling the residue with a small quantity of alcohol to remove impurities, decomposing the salt with sodium carbonate, and recrystallising the base from alcohol.

Benzoylecgonine can be easily obtained by treating ecgonine with benzoic chloride or benzoic anhydride, but the yield is not good in either case. The following method, however, gives very good results:—Benzoic anhydride (a little more than 1 mol.) is gradually added to a hot, saturated, aqueous solution of ecgonine (1 mol.), and the mixture is heated on the water-bath for about an hour. The cold product is shaken with ether to remove benzoic acid and anhydride, and the residue is rubbed and washed with a small quantity of water on the filter-pump. The yield is about 80 per cent. of the ecgonine employed. Small quantities of benzoylecgonine can be obtained by evaporating the mother-liquor, and if the filtrate is again treated with benzoic anhydride, the greater part of the unchanged ecgonine is converted into the benzoyl-derivative. The whole of the excess of benzoic acid (anhydride) employed can be obtained from the ethereal extract.

Anhydroecgonine melts at 235°, is far less readily soluble in alcohol than ecgonine, and the crystals effloresce when kept in a partial vacuum. The hydrochloride is, however, far more readily soluble in alcohol than ecgonine hydrochloride.

Cocaïne was prepared by Einhorn's method from the benzoylecgonine obtained as described above, and the preparation was found to be identical with the natural alkaloïd in every respect.

It has been observed by Lossen that, when a solution of cocaïne hydrochloride is precipitated with ammonia, the precipitate is redissolved on adding more ammonia. The authors find that this phenomenon is simply due to the additional quantity of water, and not to any solvent action of the alkali. F. S. K.

Cocaïne. By A. EINHORN (*Ber.*, **21**, 3029—3044).—*Cocaylbenzoylhydroxyacetic acid*, $C_5NH_7Me\cdot CBz(OH)\cdot COOH$, is obtained when a 3 per cent. solution of potassium permanganate (230 c.c.) is gradually added, with constant stirring, to an aqueous (1 litre of water) solution of benzoylecgonine (5 grams) and sodium carbonate. The excess of potassium permanganate is reduced with alcohol in the cold, the filtered solution carefully acidified with hydrochloric acid and evaporated; the crystalline residue is extracted with and recrystallised from alcohol, and the resulting hydrochloride decomposed by boiling with ammonia. The acid which separates from the ammoniacal solution crystallises from alcohol or hot water in large prisms, melts at 230° with decomposition, and yields benzoic acid and cocaylhydroxyacetic acid (see below) when heated with concentrated hydrochloric acid. The *hydrochloride*, $C_{15}H_{17}NO_4,HCl$, crystallises from alcohol in plates with 2 mols. H_2O, and melts at 217—218°. The *aurochloride*, $C_{15}H_{17}NO_4,HAuCl_4$, crystallises from dilute hydrochloric acid in yellow needles, melting at 228° with decomposition. The *platinochloride*, $C_{15}H_{17}NO_4,H_2PtCl_6$, separates from water in yellowish-red, nodular crystals, containing water and melting at 233°. The *methyl* salt, prepared by passing hydrogen chloride into a methyl alcohol solution of the acid, was obtained in an oily condition; it is readily soluble in water, and the solution in hydrochloric acid yields an *aurochloride*, $C_{16}H_{19}NO_4,HAuCl_4$, which crystallises in long needles, melts at 181—182°, and is sparingly soluble in water. The *ethyl* salt, prepared in like manner, is also an oil; the *aurochloride*,

$$C_{17}H_{21}NO_4,HAuCl_4,$$

separates from acidified alcohol in yellow crystals, melts at 160·5°, and is very sparingly soluble in water.

Cocaylhydroxyacetic acid, $C_5NH_7Me{\cdot}CH(OH){\cdot}COOH$, is formed in the preparation of the benzoyl-derivative, when the oxidation product is evaporated in an acid solution. It can be obtained by gradually adding a 3 per cent. solution of potassium permanganate (900 c.c.) to an aqueous ($1\frac{1}{2}$ litres of water) solution of ecgonine hydrochloride (6 grams) and sodium carbonate. The *hydrochloride*, $C_8H_{13}NO_3,HCl + H_2O$, is isolated as described above. The free *base* is obtained in the pure state by decomposing the aurochloride with hydrogen sulphide, evaporating the filtrate, recrystallising the residue from a mixture of methyl alcohol and ether, and decomposing an aqueous solution of the resulting hydrochloride with silver oxide. It separates in long needles, or in thick prisms, when ether is added to an aqueous methyl or ethyl alcohol solution, and melts at 233°. The *aurochloride*, $C_8H_{13}NO_3,HAuCl_4$, crystallises from dilute hydrochloric acid in yellow needles containing 2 mols. H_2O, and melts at 211°. It crystallises from alcohol in short, thick, well-defined prisms containing alcohol.

Anhydroecgonine can be prepared by heating cocaïne for four hours at 140° with glacial acetic acid saturated with hydrochloric acid. When anhydroecgonine is oxidised with dilute potassium permanganate, as described above, small quantities of ecgonine or cocaylhydroxyacetic acid are formed according to the conditions of the experiment. A hydrocarbon, ammonium chloride, methyl chloride, very small quantities of a secondary base, and resinous products are formed when anhydroecgonine hydrochloride is heated at 230° for a long time with glacial acetic acid saturated at 0° with hydrogen chloride. When anhydroecgonine is heated with water at 150°, it is partially decomposed into an acid and methylamine, but all attempts to prepare a simple pyridine-derivative from the base were unsuccessful.

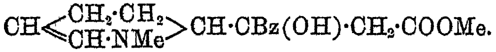
Cocaïne methiodide, $C_{17}H_{21}NO_4,MeI$, prepared by heating cocaïne (1 mol.) with methyl iodide (1 mol.) at 100°, crystallises from absolute alcohol in shining plates, melts at 164°, and is sparingly soluble in alcohol.

Cocaïne methochloride, $C_{17}H_{21}NO_4,MeCl$, prepared by treating the preceding compound with silver chloride, crystallises from a mixture of alcohol and ether in small needles or plates, melts at 152·5°, and is very readily soluble in water.

Methylanhydroecgonine methiodide, $C_{10}H_{15}NO_2,MeI$, is formed, together with benzoic acid, when an aqueous solution of cocaïne methiodide is heated at 100°. It crystallises from alcohol in slender, yellowish needles, or in well-defined prisms, and melts at 195—196°.

When cocaïne methiodide is heated at 140° with glacial acetic acid, previously saturated with hydrogen chloride, benzoic acid and a compound containing both iodine and chlorine are produced. When the last-named substance is treated with silver oxide, a crystalline, hygroscopic base is obtained.

Anhydroecgonine methiodide, $C_{10}H_{16}NO_2I$, is formed when an aqueous solution of the base just described is treated with hydriodic acid. It crystallises from alcohol or water in long prisms, containing 1 mol. H_2O, and melts at 207—208°. The constitution of cocaïne is probably



$$CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH\cdot NMe\end{matrix}{>}CH\cdot CBz(OH)\cdot CH_2\cdot COOMe.$$

F. S. K.

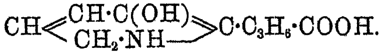
An Acid from Cod-liver Oil. By A. GAUTIER and L. MOURGUES (*Compt. rend.*, **107**, 740—743).—Cod-liver oil contains an acid in the form of an unstable compound resembling the lecithins, which decomposes in contact with acids or alkalis, and yields glycerol, phosphoric acid, and the new complex acid. Lecithins themselves are present in the oil, and add to its value by presenting phosphorus in a readily assimilable form.

The oil is systematically extracted with alcohol of 35 per cent. containing 3 per cent. of hydrochloric acid, and the solution is saturated with potassium carbonate and distilled in a vacuum at 45°. The residue is acidified, heated for a moment at 100°, and extracted with alcohol at 85°. The latter dissolves the acid, which separates as a viscid, colourless substance on cooling or on adding water. The crude product is dissolved in potash, neutralised with nitric acid, and lead acetate added so long as the precipitate is not discoloured. The lead precipitate is washed with water, decomposed by hydrogen sulphide, and the solution filtered whilst hot. The lead sulphide is washed with hot alcohol, and the washings and the original filtrate are evaporated in a vacuum. The new acid, *morrhuic acid*, crystallises in soft, yellowish, square plates of the composition $C_9H_{13}NO_3$, which differs from tyrosine by H_2 only.

Morrhuic acid has a disagreeable odour recalling that of kelp; when freshly precipitated it is oily and viscid, but it gradually solidifies. It dissolves in hot water, but separates on cooling, and is soluble in alcohol, but only slightly soluble in ether. It reddens litmus, decomposes carbonates, and forms crystallisable salts with the alkalis; its solutions give precipitates with lead and silver, but not with copper salts. Morrhuic acid also combines with acids and forms a crystalline hydrochloride, which is decomposed by water, morrhuic acid separating in the form of an emulsion; the platinochloride is soluble and crystallises in very small prisms; the aurochloride forms an amorphous precipitate which readily alters when heated.

When distilled with lime, morrhuic acid yields a base which gives with methyl iodide and potash the reaction characteristic of the pyridines. When oxidised with potassium permanganate, it yields a monobasic pyridinecarboxylic acid, which crystallises in prisms and rhomboidal lamellæ, and forms a platinochloride and an aurochloride.

The silver salt of morrhuic acid contains 2 atoms of the metal, and hence it is bibasic. The fact that it gives no precipitate with copper acetate indicates that the carboxyl is not in direct union with the pyridine-ring, and it probably has the constitution



$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CH\cdot C(OH)}\\ \mathrm{CH_2\cdot NH}\end{matrix}\Big\rangle\mathrm{C\cdot C_3H_6\cdot COOH}.$$

This formula explains the ready reduction of the silver salt even in the cold.

De Jongh's *gaduine* is probably identical with morrhuic acid.

C. H. B.

Action of Phosphorus Oxychloride on Cholic Acid. By R. CAMPANI (*Gazzetta*, **18**, 88—89).—The cholic acid employed was prepared from ox-bile by boiling it with dilute hydrochloric acid for 24 hours, and then isolating the acid in the usual way. The phosphorus oxychloride (12 grams) is added drop by drop to the cholic acid (5 grams) in fine powder; a powerful reaction takes place, and as soon as it has subsided, the product is thoroughly washed with boiling water, and allowed to dry at the ordinary temperature. It is a greenish-yellow powder, very sparingly soluble in alcohol, but easily in ether; this, on evaporation, leaves it as a brown, amorphous, vitreous residue. On analysis, it gave numbers corresponding with the formula $C_{24}H_{36}O_3$. It is insoluble in aqueous alkaline solutions, but on long boiling with alcoholic potash it dissolves and is reconverted into cholic acid, which is precipitated from the solution on adding hydrochloric acid. The compound, therefore, is the anhydride of cholic acid.

C. E. G.

Gelatinous State of Albuminoïd Substances. By V. MICHAILOFF (*J. Russ. Chem. Soc.*, 1887, **19**, 666—690; 1888, **20**, 35—72, 159—179, 274—360, 380—388).—After giving the history of this and similar subjects (colloïdal matters in general), the author shows the conditions under which white of egg from different sources exists in various solutions, precipitates, and gelatinous coagulates, and in coagulates obtained by heat, how these different modifications are formed and transformed, and describes at some length their properties (chemical and physical), especially those of Tarchanoff's "tata-albumin" and its behaviour towards solutions of different salts at different temperatures, as well as the results obtained on dialysis (see Abstr., 1887, 856). The mutual actions of different kinds of albuminoïd substances are also studied, and it is shown that albumins are acid, and globulins basic compounds. Gelatinisation of albumin in the first phase is due to hydration; in its subsequent phases to dehydration, which is more or less complete according to the conditions. B. B.

Physiological Chemistry.

Primary and Secondary Oxidation. By O. NASSE (*Pflüger's Archiv*, **41**, 378—389).—A distinction is drawn between direct oxidation (oxidation occurring at the body temperature in the blood and fluids of the body by neutral oxygen combining with some readily oxidisable matter), primary oxidation (such as occurs in the body chiefly; the complex molecules are first altered by some ferment action in order to render them readily oxidisable), and secondary oxidation (oxidation of products of metabolism which have been formed by other processes than oxidation). The influence of readily oxidisable substances, such as fat and phenol, given in the food, on secondary oxidation was investigated, the urine being examined for ethereal hydrogen sulphates and glycuronic acid; it was found that the burning of fat in the organism furthers secondary oxidation processes, as is shown by the rise in the amount of ethereal hydrogen sulphates and fall in the glycuronic acid on the days on which fat was given with the food. W. D. H.

The Influence of Light on Oxidation in Animals. By J. LOEB (*Pflüger's Archiv*, **42**, 393—407).—The comparison of plants with animals has suggested the question whether light influences the chemical processes in animals as, according to several experimenters, it does in those plants which contain chlorophyll. Moleschott (*Wien. med. Wochensch.*, 1885) found in frogs that more carbonic anhydride was produced in the light than in the dark. But here no observations were made as to whether the animals moved much or little during the experiments. In the light, animals are more stimulated to movement, and muscular activity alone might thus explain the increased production of carbonic anhydride. v. Platen (*Pflüger's Archiv*, **11**, 272) observed also an increase in gaseous metabolism, and found, moreover, that the illumination of the retina by light also produced, apparently reflexly through the central nervous system, a similar effect. Speck (*Arch. f. exp. Path. u. Pharmak.*, **12**), however, arrived at the conclusion that in the human subject, light of itself produces no increase in oxidation processes. On the local action of light on tissues removed from the body, but still retaining some vitality, the experiments recorded by Fabini and others are unsatisfactory and inconclusive, very little care having been taken to avoid putrefaction, and even if this had not occurred the tissues were dying, and not living healthily. Moreover, the influence of changing atmospheric temperature seems also to have been neglected.

In the present research, these sources of error were avoided by taking lepidopterous larvæ in the chrysalis stage when movements are practically absent. A number of these were weighed and placed in a closed glass vessel within a beaker of water, and exposed to diffused daylight. Others were exactly similarly treated, except that instead of water, a solution of nigrosine of the same temperature was used, so that they were in darkness. At the end of the experiment, they were again weighed; those which had lost most weight would be those which had undergone most active oxidation; but in case some individual peculiarities of the pupæ themselves might have produced these effects, a control experiment was performed by reversing the conditions; those which before were in the light were now put in the dark, and *vice versâ*.

From a number of experiments the conclusion was finally drawn that light produces in these animals no increase of oxidation processes; that light has in fact no influence at all on these processes. These simple experiments were fully confirmed by more complex ones in which analyses of the oxygen used and carbonic anhydride produced were measured.

This negatives the idea that light has any local action on animal tissues, although it does not at all contradict the conclusion that light may have an indirect effect on animals with intact central nervous system and active muscles, probably in this case a reflex effect through the optic nerves or sensory nerves of the cutaneous surface.

W. D. H.

The Melting Point and Chemical Composition of Butter as Effected by Nutrition. By A. MAYER (*Landw. Versuchs-Stat.*, 1888, 261—282).—The examination of butter produced by cows under various conditions was undertaken to explain if possible why Danish butter has a better sale than Dutch in the English markets. All that was known on the subject was that the Danish is harder and of a better colour. Inquiries showed that whereas in Holland the cows were fed on pasture and calved in spring, in Denmark they, for the most part, drop their calves late on in the year, and are house fed. The cows under examination were fed at various periods on roots, hay, grass, clover, and silage, and the analysis of the butter produced showed that the percentage of volatile acids varies as the specific gravity; that the melting point does not march parallel with specific gravity, but is dependent on the percentage of the oleïns, butyrin, capronin, &c., present; the percentage of volatile acids and the specific gravity of the butter produced by any one cow varies more considerably than is generally supposed when the experimental conditions are changed: the percentage of volatile fatty acids is dependent on the period of lactation, rising as the period progresses, but it is also dependent on the feeding, being highest when roots, meadow-grass, and clover are given, and lowest with ensilage: on the contrary, ensilage and hay produced a butter of high melting point, whilst grass or clover, whether as pasture or given out in the house, lowers the melting point: the solidifying point follows the melting point, rising and falling with it. E. W. P.

Proteïd Metabolism in Man. By F. Hirschfeld (*Pflüger's Archiv*, **41**, 533—565).—The following are the final conclusions drawn by the author from his research. It is possible for a healthy man (in one case for 15 days, in another for 10 days) to maintain a nitrogenous balance and equal body weight on from 5—8 grams of nitrogen daily: this corresponds to 30—35 grams of proteïd; or if one excepts the days on which very little nitrogen (5 grams) was taken, the conclusion that 35—40 grams of proteïd *per diem* is sufficient can certainly be drawn. Whether this would be possible for periods longer than those mentioned cannot be stated.

This is contrary to the generally received opinion that an adult man requires 100—120 grams of proteïd daily, and that it is dangerous to ingest less, or else the tissue-proteïds will be disintegrated. On the contrary, so much proteïd as this increases the tissue-proteïd (unless great activity compensates for this hypertrophy), and the fat of the organism also increases. W. D. H.

Glycogen. By E. Neisser (*Chem. Centr.*, 1888, 1083, from *Centr. Physiol.*, 1888, 141—142).—The author conducted experiments with mice fed with about 80 different sorts of food in order to determine the extent to which the glycogen of the liver is affected by them. Morphine, amygdalin, and mytilotoxin appear to cause an accumulation of glycogen. The health of the animals was no doubt of considerable influence on the amount of glycogen, although in one case, that of a mouse fed on mytilotoxin, and seriously ill, the liver contained a considerable quantity of glycogen, whilst, on the other hand, with several animals fed on papaïn, asparagine, coniferin, coumarin, and in perfect health, the liver contained no glycogen.

J. W. L.

Synthetical Processes in the Animal Organism. By E. Pflüger (*Pflüger's Archiv*, **42**, 144—154).—A living liver free from glycogen will again form that substance, not only from carbohydrates but from glycerol, gelatin, or proteïd. v. Mering fed dogs on phloridzin, whereby they became diabetic, and in a few days all carbohydrate material in the body had been discharged in the urine as sugar. If now the same drug was given to the same animals after a few days' interval, during which they had no food, they once more became intensely diabetic, and the quantity of sugar passed was so enormous that it cannot be supposed to have come from the drug itself (*Verhandl. VI Congresses inneres Med. Wiesbaden*, 1887). One explanation of the way in which glycogen is formed after the administration of glycerol, is the well-known "economy theory," another is that glycerol and like substances act as stimuli to liver activity. It certainly cannot be supposed that glycogen is directly formed from the substance administered—or at least not in all cases; for instance, from ammonium carbonate. The question then arises as to the genetic relationship existing between glycogen and albumin. Experiments on the decomposition products of proteïds have in no case yielded a carbohydrate; and not only that, but proteïds never yield any of the decomposition products of carbohydrates (lactic acid, mucic acid, tartaric acid, &c.). Still, we have the formation of glycogen taking place in the liver when no food but albuminous food is taken.

The following general considerations will, however, lead to a better understanding of the subject. The chemical differences between animal and vegetable cells are not so great as was at one time supposed. Their chemical composition, so far as it is known, is the same; all living cells breathe oxygen, and produce carbonic anhydride, water, and amido-compounds. If the synthetic processes are more highly developed in chlorophyll-holding plants, that does not mean that synthetic processes are absent from animal cells. As instances of synthetic processes in animal cells, the formation of hippuric acid from glycocine and benzoic acid, or of ethereal hydrogen sulphates from phenol and sulphuric acid, may be taken. A special kind of synthesis must, moreover, occur in the retrogressive metamorphoses of proteïds which lead to the formation of uric acid and members of the same group. In albumin itself, and in the products of albumin obtained outside the body, the number of carbon-atoms is much greater than that of nitrogen-atoms (indole, leucine, tyrosine, &c.); but in these products of metamorphoses in the body, the nitrogen and carbon-atoms are nearly equal in number, or, as in the cases of urea and guanidine, the nitrogen-atoms are the more numerous. The importance of such synthesis occurring in living cells, resulting in the formation of cyanogen containing molecules, has been before insisted on by the author.

Researches on the formation of fat within the body show that here again there are undoubtedly syntheses occurring as the result of the activity of living cells: in fact, reactions occur which cannot be repeated in the laboratory or explained by any known chemical laws; they are probably, therefore, the result of a breaking down of molecules in the first place, and the living cells then building up entirely new materials of a complicated nature from the simple carbon compounds so liberated.

The carbohydrates, for example, are derivatives of the hexatomic alcohol $C_6H_8(OH)_6$. But by feeding an animal on starch, the fat of the body is increased, and substances containing chains of 16 to 18 atoms of carbon linked one to another are formed; and in the case of stearic acid at least, we have a number (16) which is not a multiple of 6. By this synthesis, too, we have substances which possess the property of circular polarisation changed into those which are optically inactive. The first change must, however, be a process of reduction; metabolic changes must occur, and no nutrient material stimulates metabolism like proteïd; this explains why feeding on starch mixed with a small amount of proteïd produces fat, and without it will not. The proteïd admixture is, however, so small that it alone will not explain the great increase in fat. In other parts of the animal kingdom, there are similar occurrences; for instance, the formation of beeswax from honey. Another sample of the same kind is the formation of fat from proteïd, although this is not so well proved as the foregoing cases. In the synthesis of fat from carbohydrate, the group $CH{\cdot}OH$ must be changed into CH_2; and in the formation of carbohydrate (glycogen) from proteïd, the group CH_2 must be changed into CH·OH; in both cases, numbers of these groups become linked together.

The close resemblance between animal and vegetable cells is further shown by the fact that many lower plants (bacteria, moulds, &c.) not only flourish in solutions of albumin and sugar, but actually shed out ferments to convert proteïd into peptone, and starch into sugar, and thus aid absorption. They breathe oxygen, produce carbonic anhydride, amido-derivatives, and, without the aid of sunlight, fat, carbohydrate, and proteïd. Nägeli (*Sitzber. Bair. Akad. Wissensch.*, 1879) has, however, shown that these fungi will assimilate carbon from compounds in which it is combined with hydrogen (amines, &c.), but not from those where it is combined with nitrogen (cyanogen).

W. D. H.

The Sugar-contents of the Horse's Stomach. By ELLENBERGER and HOFMEISTER (*Pflüger's Archiv*, **41**, 484—489).—Seegen (Abstr., 1888, 171) has commented on the small quantities of sugar found in the stomach and intestines, and considers that this may be explained by its rapid absorption immediately it is formed.

The authors state that although a similar state of things may occur with peptone formed from albuminous food, it is certainly not the case in horses and pigs fed on starchy food. The quantity of sugar in the alimentary tract of these animals varies, but they have found from 1 to 3·5 per cent. of sugar (30—150 grams) in the stomach of the horse, and from 0·6 to 0·8 in the stomach of the pig.

The conditions on which the varying amount of sugar depends are:—(1) Length of time after meal: the highest amount is present 1 to 1½ hours after a meal; (2) abundance or otherwise of hydrochloric acid in the gastric juice, which stops the conversion of starch into sugar; (3) condition of the starch in the food, whether cooked or uncooked, corn or potatoes, &c.; (4) another condition which must not be overlooked is the difference of secretion in different parts of the stomach, and if the contents are not properly mixed, more sugar will be found in one part than another (Abstr., 1886, 952; 1887, 743, 744). Seegen appears to have killed his animals too late, 3½—13 hours after a meal.

W. D. H.

Post-mortem Formation of Sugar in the Liver. By H. GIRARD (*Pflüger's Archiv*, **41**, 294—302).—The table (p. 177) gives the results of estimations of the percentage of sugar and glycogen in pieces of the liver, at varying periods after death.

These figures show that the increase in sugar corresponds with the decrease in glycogen; and the conclusion drawn is that the sugar is formed from the glycogen. This conclusion is contrary, however, to the belief of Seegen, who considers that sugar is formed from peptone.

In addition to this, the following facts were also made out:—That the power of liver cells to change a solution of glycogen into sugar is not destroyed after death, even though disease may, during life, have deprived the liver of all its glycogen. The presence of blood in the liver assists in the process. Other tissues, such as muscles which

Animal.	10 minutes after death.		24 hours after death.		48 hours after death.	
	Sugar.	Glycogen.	Sugar.	Glycogen.	Sugar.	Glycogen.
Dog, 1	0·55	2·12	1·80	0·76	1·75	0·75
„ 2	0·74	4·05	3·00	1·50	3·12	1·38
„ 3	0·95	4·73	3·50	1·80	3·73	1·45
„ 4	0·86	3·56	3·35	0·80	3·30	0·67
Cat, 1	0·48	5·88	2·95	3·20	3·06	2·88
„ 2	0·62	4·96	3·15	2·08	3·48	1·87
Rabbit	0·75	9·56	3·58	6·35	3·85	4·28
„	0·65	10·25	4·12	6·24	4·20	5·05

contain glycogen, have a similar property, namely, their glycogen is transformed after death into sugar; a solution of glycogen placed in contact with the muscle, especially when blood is present also, is similarly acted on.

If the liver is deprived of glycogen by disease, no sugar is formed in it after death. The liver, after death, moreover, does not possess the property of changing peptone into sugar. W. D. H.

Aqueous Humour. By Kuhn (*Pflüger's Archiv*, **41**, 200—202). —Contradictory statements have been made as to the presence or absence of grape-sugar in the aqueous humour. In the present experiments, the aqueous humour of the rabbit and ox was used; the humour was withdrawn from the anterior chamber of the eye by a Pravaz syringe, and the amount drawn from a single eye was sufficient to show, with Trommer's test, that a substance is always present which reduces copper oxide. This cannot be alcaptone (catechol), as it is not precipitated by lead acetate. It also reduces mercury. Two quantitative estimations were made with large quantities of the fluid, by means of the saccharimeter; the result in one case gave a percentage of 0·044 sugar, in the other 0·033. W. D. H.

Lactic Acid in Pale and Red Muscles. By W. Gleiss (*Pflüger's Archiv*, **41**, 69—75).—Pale muscles from the frog and the red muscles from the tortoise were tetanised to equal extents; their acidity was then tested with litmus, the intensity of the change in colour being taken as a measure of the amount of acid present. In some cases the degree of the yellow tint, produced by lactic acid in dilute solutions of ferric chloride, was used as the test. It was found that the quickly contracting muscles of the frog became acid much sooner, and to a greater extent, than the slowly-contracting muscles of the tortoise. This was found to be a general rule throughout the animal kingdom; if such a muscle as the *gastrocnemius* (pale) of a rabbit and the *soleus* (red) of the same animal were compared in the same way again, the more active muscle was the more acid.

With regard to the formation of sarcolactic acid during *rigor mortis*, no difference between the two sets of muscles could be made out.

W. D. H.

Citric Acid in Cow's Milk. By SOXHLET (*Chem. Centr.*, 1888, 1067—1068; see also *Landw. Versuchs-Stat.*, **35**, 351—436).—Henkel has estimated the amount of citric acid in cow's milk in the author's laboratory, and finds it contains 0·9 to 1·1 gram per litre. This quantity is by no means a small one, being equal in amount per day per cow to that contained by 2 to 3 lemons. The author calculates that the cow's milk of Bavaria annually contains 40,000 centner (= cwt. approx.) of citric acid. Condensed milk frequently contains crystals of calcium citrate.

J. W. L.

Glycollic Acid and Pyrotartaric Acid from Suint. By A. BUISINE and F. BUISINE (*Compt. rend.*, **107**, 789—791).—Glycollic and pyrotartaric acids exist in suint in the form of potassium salts, and are separated from that portion of the suint acids which dissolves in water, alcohol, and ether. After separation of barium malate and the removal of the excess of barium, the solution of the free acid is agitated with washed lead hydroxide, which precipitates basic lead glycollate, whilst pyrotartaric and lactic acids remain in solution.

Glycollic acid constitutes about 1 per cent. and pyrotartaric acid about 0·2 per cent. of the dry residue from suint.

C. H. B.

Fate of certain Ferments in the Organism. By H. HOFFMAN (*Pflüger's Archiv*, **41**, 148—176).—The result of this investigation are as follows:—

1. In normal human urine, there are varying quantities of pepsin and diastatic ferments present. The amount of these ferments in the urine is related to the intake of food. This point is thoroughly worked out, and tables and curves are given of the relative amount of pepsin in the urine in connection with the time of day and times of meals.

2. Urine has no power, or hardly any, to destroy pepsin or diastatic ferments.

3. Normal human urine contains no trypsin.

4. Normal human urine easily destroys small quantities of trypsin.

5. Very large quantities of trypsin are not destroyed by urine.

6. If the flow of the pancreatic secretion into the intestine be hindered or prevented, trypsin appears abundantly in the urine.

7. Trypsin is found in the liver, spleen, and kidneys of various animals. This will perhaps explain Herzen's observation, that a mixture of spleen and pancreas undergoes self-digestion more quickly than the pancreas alone; the action is a cumulative one.

W. D. H.

Composition of Pearls. By J. HARLEY and H. S. HARLEY (*Proc. Roy. Soc.*, **43**, 461—465).—A quantitative analysis of oyster pearls gave the following results:—Calcium carbonate, 91·72 per cent.; organic matter (animal) 5·94 per cent.; water 2·23 per cent. The proportions are quite different from those in mother-of-pearl. Pearls are not soluble in vinegar unless pulverised. A cocoanut pearl gave on analysis the same constituents as oyster pearls, but its origin was doubtful. Human pearls gave water 2·05 per cent., solids 97·95 per cent.; the solids containing cholesterin, 98·63 per cent., animal matter 1·37 per cent. Hence they appear to be pure cholesterin biliary concretions.

H. K. T.

Myxœdema. (*Clinical Soc. Trans.*, Supp. to vol. xxi.)—This volume is a report of a Committee appointed to investigate the disease known as myxœdema. The section relating to the chemical investigation of the tissues and organs from cases of the disease in human beings, as well as that produced artificially in animals by the removal of the thyroid body, contains analyses by Drs. Stevenson, Bernays, and Halliburton. The other sections of the report are of clinical interest.

Charles (*Medico-Chirurg. Trans.*, **61**, 62) stated that in the case examined by him, the skin yielded 50 times more mucin than normal skin does; hence the name myxœdema given to the disease.

Subsequent investigations have not confirmed this. The method consisted in extracting the tissue with lime-water (or diluted baryta-water), and then precipitating the mucin dissolved out by this reagent with excess of acetic acid. This precipitate was collected, washed, dried, and weighed. It is not a method which is absolutely accurate, but it gives fairly good comparative results. The following were the average percentages obtained with normal tissues:—

Skin (children)	0·766
Skin (adults)	0·385
Connective tissues	0·521
Parotid	traces.
Heart tendons	

In cases of human myxœdema, although there were instances of increase in the amount of mucin in the skin, the average of 10 analyses gives a number (0·374 per cent.) which is approximately the same as in normal adult skin. With regard to other organs, there was also noted a slight occasional increase; the most marked, however, was in the case of the tendons, especially the heart tendons, the average of five analyses giving a percentage of 1·5.

Mucin is not only, however, a constituent of the ground substance of connective tissue, but it also results from the degeneration of protoplasm as in the goblet cells of mucous membranes, and the acini of the mucous glands. In one case, the parotid gland was found to contain a large increase of mucin; it normally secretes a clear saliva containing no mucin. This is the only case in which the secreting glands were examined, and the result is interesting, as it coincides with what is seen in the disease produced in monkeys artificially. Monkeys show the disease very typically, and the increase of mucin can also be demonstrated better than in the human subject; for in late stages of the disease in man when white fibres or fat cells have permeated the new connective tissue, the increase of mucin is not at all marked; in early stages, it appears to exhibit a percentage of mucin like that found in the not fully developed tissues of very young children. Certain classes of animals do not show the typical characteristics of the disease.

The following table illustrates the quantitative results as obtained in monkeys :—

Animal.	Mucin in parts per 1000.				
	Skin.	Tendon.	Parotid.	Submaxillary.	Blood.
No. 1A. Normal......	0·89	0·39	0	—	0
No. 9. „	0·9	0·5	0	trace	0
No. 1. 55 days after operation......	3·12	2·55	0·72	6·0	0·35
No. 3. 32 days after operation......	—	—	—	—	trace
No. 5. 49 days after operation......	2·3	2·4	1·7	3·3	0·8
No. 10. 7 days after operation......	0·45	0·904	trace	0·16	trace

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Bacterio-purpurin. By T. W. ENGELMANN (*Pflüger's Archiv*, **42**, 183—186).—In *Pflüger's Archiv* (**30**, 95) the author has previously described a bacterium producing a red pigment, to which he gave the name *B. photometricum*, as light by varying the amount of red pigment influences its movements. Since then he has made a number of observations on different varieties of bacteria which produce a red colour. All belong to the class of sulphur-bacteria (Winogradsky, *Botan. Zeit.*, 1887, No. 31—37); that is, bacteria which in the presence of free hydrogen sulphide, oxidise sulphur, forming sulphuric acid; all these bacteria are moreover coloured by a purplish-red pigment diffused through their protoplasm—bacterio-purpurin (Ray-Lankester); they are all also influenced by light like the *B. photometricum*. This last point distinguishes them from certain colourless sulphur-bacteria.

Different coloured lights affect the bacteria differently; the most powerful being the ultra-red, the yellow, and part of the green. These are the places in the absorption-spectrum of bacterio-purpurin where the greatest absorption of light occurs. A table is given of the amount of absorption of light of bacterio-purpurin measured by the spectrophotometer for the different part of the spectrum. Absorption and physiological effects are thus closely related to one another.

This fact suggested a comparison between this pigment and chlorophyll; and it was then found that bacterio-purpurin is a chromophyll, absorbing carbonic anhydride, and giving out oxygen in the light; sunlight produces this most readily, but the ultra-red works only a little less efficiently than mixed light. W. D. H.

Beer Yeast. By MARTINAND (*Compt. rend.*, **107**, 745—748).—Observations of the time required to form acrospores do not yield results sufficiently precise to distinguish between different species of *saccharomyces*. Experiments in which various species of *saccharomyces* were allowed to act on sterilised solutions of maltose for several days, show that *S. cerevisiæ* from beer yeast acts more rapidly and completely than *S. ellipsoideus*, *S. pastorianus*, and *S. apiculatus*. The times required for the formation of acrospores were somewhat variable.

With a solution of saccharose inverted by hydrochloric acid, *S. cerevisiæ* and *S. pastorianus* were found to act less completely than *S. ellipsoideus*.

Further experiments are required before these observations can be utilised for the practical analysis of yeast. C. H. B.

Yeast-poisons. By H. SCHULZ (*Pflüger's Archiv*, **42**, 517—541).—Previous researches by the author (*Virchow's Arch.*, **108**, 427) have led him to the conclusion that drugs produce their effect by raising or lowering the physiological processes in animal cells; and that small and large doses of any one drug may produce opposite effects of this kind.

The same thing occurs with vegetable cells, the various substances that, in large amount, produce stoppage of fermentations, produce, when excessively dilute, an increase of the activity of the yeast organisms as measured by the amount and pressure of carbonic anhydride produced.

The apparatus used for the investigation is fully described, and the results set out in detail, the pressure of carbonic anhydride being represented graphically in the form of curves.

The results, however, may be briefly summarised in the following way for each of the various drugs used:—

Mercuric Chloride.—The increase of activity of the yeast showed itself most when the amount of dilution was about 1 : 500,000.

Iodine.—Here the optimum was reached when the dilution was 1 : 600,000 in one series of experiments; 1 : 100,000 in another.

Bromine.—Here two sets of experiments both yielded the dilution 1 : 300,000 as the most favourable for ferment activity.

Arsenious Acid.—The relation found here as the best was somewhat less than in the foregoing cases; the proportion of 1 : 40,000 gave the most vigorous production of carbonic anhydride: a dilution less than this, 1 : 50,000, produced no effect whatever.

Chromic Acid.—This had to be used still more concentrated; a dilution 1 : 8000 producing the most marked stimulating effect on the micro-organisms.

Salicylic Acid.—The optimum of dilution was here 1 : 4000; and in the case of *formic acid* 1 : 10,000. W. D. H.

Blood Pigment as a Gauge of Gaseous Exchanges in Plants. By T. W. ENGELMANN (*Pflüger's Archiv*, **42**, 186—188).—The principle of this method is not new, as Hoppe-Seyler showed (*Zeit. physiol. Chem.*, **2**, 425) that a piece of living *Elodea canadensis* in diluted decomposing blood will in direct sunlight cause the venous colour to become arterial, while in the dark the venous colour returns. But this same fact may also be used for microscopical investigations of living cells or small particles of living plant tissues, and as a test for chromophylls. A small spray of spirogyra was mounted on a drop of diluted defibrinated ox blood, which had been rendered venous by a stream of hydrogen or carbonic anhydride. In 10—15 minutes in diffuse daylight, in one minute in direct sunlight, the blood in the neighbourhood of the green fragment had become arterial, while in the dark it once more returned to its venous tint. The same change may be watched with a spectral ocular, or better a microspectrophotometer; the one band of hæmoglobin giving place to the two of oxyhæmoglobin, or the reverse.

The change occurs at different rates under the influence of light from different parts of the spectrum:—A spectrum was projected under the preparation; the change to the arterial tint occurred in that part of the spray of the spirogyra which was lying over the outermost part of the visible red, reaching its height, however, about the C line, and then sank until the beginning of the green was reached. Sometimes a second effect was seen in the blue-green, and a slighter one in the violet. Other chromophylls (for instance, bacterio-purpurin, see p. 180) act *mutatis mutandis* similarly to chlorophyll.
W. D. H.

A Plant which Destroys the Sense of Taste for Sweets and Bitters. By B. BERTHOLD (*Chem. Centr.*, 1888, 1071, from *Centr. Med. Wiss.*, 1888, 460—461).—This drug comes from an Asclepiadea, *Gymnema sylvestre*, found in Assam, on the Coromandel coast, and on the African continent, and is a strong woody shrub with long thin branches. The Hindoos have used the pulverised bark for a long time as an antidote against snake bites. When chewed, the leaves possess at first a bitter astringent, later a slightly acid taste. Directly after chewing, one loses the power of taste for sweet and bitter principles, but only for these two effects on the sense of taste. Sugar tastes like sand and quinine sulphate like chalk. At the end of 1—2 hours, the normal sense of taste is recovered. The author has commenced the chemical investigation, and has succeeded in separating three substances, but these are not yet sufficiently characterised.
J. W. L.

Occurrence of Aluminium in Vascular Cryptogams. By A. H. CHURCH (*Proc. Roy. Soc.*, **44**, 121—129).—More recent analyses generally recognise the presence of alumina in plants as adventitious. The author has, however, found it to be an important constituent of many Lycopodiæ, for instance, *L. alpinum*, *L. clavatum*, *L. selago*, and *L. cernuum*, whilst in *Selaginella spinulosa* it is absent. The earth is also absent in *L. phlegmaria* and *L. billardieri*, but these were afterwards found to be epiphytic. Plants closely related to the

Lycopodiæ, namely, *Equisetum*, *Ophioglossum*, *Salvinia*, *Marsilea*, *Psilotum*, and *Selaginella*, gave negative results. Of tree ferns, *Cyathea serra* gave negative results, whilst the ash of an unknown tree fern from New Zealand contained 19·65 per cent., *Cyathea medullaris* from the same source examined qualitatively gave abundance of alumina, as also did *Alsophila australis* and to a less extent *Dicksonia squarrosa*. Alumina is also an important constituent of the water-moss, *Fontinalis antipyretica*. The alumina in the Lycopodiæ occurs in combination with organic acids. It may serve to neutralise the acids produced in the plant. It is noticeable that the essential inorganic constituents of plants have low atomic weights, and fall within series 1, 2, 3, and 4 of the periodic arrangement. H. K. T.

Formation of Nitric and Nitrous Acids by the Evaporation of Water in Presence of Alkalis and Soil. By A. BAUMANN (*Landw. Versuchs-Stat.*, 1888, 217—264).—Schönbein (*Annalen*, **124**, 4) and others have stated that when water is evaporated, ammonium nitrate and nitrite are produced. They also stated that calcium carbonate as well as hydrated oxides absorb ammonia and convert it into nitrates. The author has made numerous experiments, all of which he here details, and brings forward conclusive evidence that all these experiments made by Schönbein are incorrect. He firstly attributes the false results to the absence of the delicate reagents now at hand, whereby ammonia, nitrates, nitrites, and ozone, and hydrogen peroxide may be detected. Secondly, he shows that the source of nitrates is the gas flames used for evaporation, and for heating water-baths, &c., and that when evaporation is conducted without the direct aid of gas flames, for instance, by sun heat, or previously heated sand-baths, no trace of nitrates is found, if the evaporation is conducted in a room where no gas flames have been burning. He further shows that most of the chemical preparations which are sold as pure contain nitric acid, and he instances a case in which to prepare pure calcium carbonate by precipitation, one portion of the product was dried in a water-bath, the other portion by filter-paper, the former product contained nitrate, the latter none. This holds good for all reagents similarly prepared. It is also shown that even the very tests employed to detect nitric acid, such as brucine, may and frequently do contain a trace of nitrate.

Passing on to Franks' experiments on the disappearance of the ammonia when ammonium chloride is mixed with soil, he points out that Frank seems to have forgotten the action of alkalis on compounds of ammonia, and shows that in forest soils nitrates are not found, nor are they produced from added ammonia. Finally, he warns all who are experimenting on nitrification to beware lest they introduce nitric acid by heating their solutions over gas flames, or ignite solids in open crucibles, &c., also that chemicals or samples must not be kept in rooms where gas is burning, or they will be more or less contaminated. E. W. P.

Composition of Spring Wheats grown in 1887. By M. MÄRCKER (*Bied. Centr.*, 1888, 708—715).—This is a similar paper to the following, in which the compositions of varieties of foreign wheats are compared. It appears that, generally, the highest percentage of albuminoïds and gluten is to be found in those wheats which come quickest to maturity (under 130 days), when there would be, of albuminoïds, 13·17 per cent., and of dry gluten, 18·08, whereas when the period of growth exceeds 130 days, the albuminoïds amount to only 12·47, and gluten to 9·22 per cent.; the smaller the grain, the higher the percentage of gluten, whilst a large grain is indicative of a high percentage of starch; the wheats richest in gluten produce a more bulky dough than other kinds, and the early ripened wheat and the largest grains are most suitable for baking purposes. The greater the percentage of gluten, the higher will the dough made from the flour rise in the aleurometer. E. W. P.

Composition of East Indian Wheat. By T. DIETRICH (*Landw. Versuchs-Stat.*, 1888, 309—318).—Several varieties of Indian wheat are fully described, both physically and chemically. On comparing the percentage of albuminoïds, it is found that the mean of 937 analyses of English, Russian, &c., wheats gives 13·90 of crude albuminoïds in the dry substance, whilst the Indian wheats contain only 12·66 per cent. as a mean. E. W. P.

Composition and Nutritive Value of Oats. By M. MÄRCKER (*Bied. Centr.*, 1888, 697—704).—From a number of analyses and experiments on several varieties of oats, the details of which are given, the following conclusions are drawn:—The heavier-yielding sort is poorer in albuminoïds than the lighter-yielding; there is no definite ratio between the percentages of fat and albuminoïds; that sort which comes quickest to maturity is richest in albuminoïds; the grain poorest in albuminoïds has the lowest bushel-weight, and the largest individual grains are also the poorest in nitrogen; the coefficient of digestion does not seem to be influenced by the composition. Those grains which are smallest in size and richest in nitrogen have most hull, and generally this hull is poorer in albuminoïds than that of other grains. The thickness of the skin surrounding the seed, measured immediately above the embryo, is not invariable—in one year it may be thickest in the large grains, whilst in other years it is thinnest. A table is also given representing the germinative power and total yield of nutrients per acre, but with one or two exceptions the oats are of foreign kinds and not grown in England. E. W. P.

Calcium Sulphite as a Preventative of Loss of Nitrogen in Manure Heaps. By E. JENSCH (*Chem. Zeit.*, 12, 354—355).—The author draws attention to the enormous losses of nitrogen inherent to the present system of storing farmyard manure. These losses can be reduced by spreading gypsum, superphosphate and gypsum, and kainite on the manure; but such additions are superfluous from a manurial point of view in many districts, therefore those means have not met with extensive application. Calcium sulphite is now recommended for the purpose; it is inexpensive, can be applied everywhere, and not only retains ammonia, but also acts as a disinfectant. It is obtained as a bye-product from the gases evolved from the roasting of zinc-blende, and is specially prepared for the present purpose free from lime and calcium carbonate, and with an ammonia-absorbing efficiency of 85 per cent. as compared with 68 per cent. in the best commercial unburnt gypsum. Its action as a manure on vegetation has yet to be tested. D. A. L.

Analytical Chemistry.

Gas Analysis. By H. DREHSCHMIDT (*Ber.*, **21**, 3242—3251).—The author describes a new apparatus for gas analysis similar to Hempel's (Abstr., 1887, 1062) but somewhat improved. A sketch of the apparatus is given and also examples of the results obtained by it.

N. H. M.

Estimation of Iodine. By W. STORTENBEKER (*Rec. Trav. Chim.*, **7**, 141—151).—The estimation of iodine in its compounds with chlorine may readily be effected, according to Bornemann, by decomposing the solution with potassium iodide and estimating the liberated iodine: $ICl_x + xKI = xKCl + (1 + x)I$. The author does not, however, find this method satisfactory, especially in cases where the value of x is high. This is also the case with the method proposed by Duflos of distilling with an oxidising agent (in this case a ferric salt and potassium iodide), when the whole of the iodine should pass over into the distillate. The author, therefore, proposes the reaction $2xFeSO_4 + xH_2SO_4 + 2ICl_x = xFe_2(SO_4)_3 + I_2 + 2xHCl$, which is complete as long as excess of the ferrous salt is carefully avoided or if a mixture of both a ferrous and a ferric salt is used. All that is necessary is distillation and determination of the iodine in the distillate.

The same method may also be used in estimating iodic acid, since $2HIO_3 + 10FeSO_4 + 5H_2SO_4 = I_2 + 6H_2O + 5Fe_2(SO_4)_3$, but in this case also, excess of ferrous salt must be most carefully avoided.

H. C.

Estimation of Nitrogen in Nitrate-superphosphate and in Chili Saltpetre. By P. ZIPPERER (*Chem. Zeit.*, **12**, 955 and 987—988).—The author confirms what has been advanced by others, namely that carefully prepared nitrate-superphosphate, containing no free sulphuric acid, suffers no loss of nitrogen even at 100°. But in the manufacture of nitrate-superphosphate, it is found advantageous to use a slight excess of sulphuric acid, and such superphosphates lose nitrogen on heating, in amounts varying with the quantity of free acid, the bulk of solution heated, and the duration and degree of heating. Hence Grandeau's method of evaporating a measured quantity of the solution gives low results, and to avoid this source of error the following plan is suggested:—If the substance contains 2 to 4 per cent. of nitrogen, take 20 grams, if 6 per cent. 14 grams, and if 8 per cent. 10 grams, treat in the usual way for dissolving in water, and make up to 1 litre; neutralise 500 c.c. with sodium hydroxide (free from nitrate), and make up this solution to 1 litre. 50 c.c., or in case of a superphosphate containing only 2 per cent. of nitrogen, 100 c.c., of the neutralised solution is evaporated to dryness and then examined by the Schloesing-Grandeau method or with the nitrometer. The latter plan the author finds as accurate as the former, and describes a slightly modified apparatus and the mode of using it. For the analysis of nitrate, the author takes a measured quantity of a dilute solution, in preference to a weighed quantity of a concentrated solution, and determines in the nitrometer. D. A. L.

Estimation of Phosphoric Acid. By A. STUTZER (*Chem. Zeit.*, **12**, 492).—The drawbacks to the method of estimating phosphoric acid in manures, &c., by direct precipitation with magnesia mixture in presence of ammonium citrate, are the length of time required for the complete precipitation, the inconvenience of the prolonged stirring, and the danger of scratching the sides of the vessel so that the ammonium magnesium phosphate becomes firmly attached to the glass. To avoid these difficulties the author adds a small quantity of ashless filter-paper, pulped to a thick magma in ammonia, previous to stirring for five minutes with a mechanical stirrer; the ammonium magnesium phosphate may then be at once collected. In addition to the great saving of time, 10 beakers may be stirred at once.

D. A. L.

Wiborg's Gasometric Method for estimating Carbon in Iron and Steel. By H. v. JÜPTNER (*Chem. Centr.*, 1241—1242, from *Österr. Zeit. Berg. Hüttenwesen*, **34**, 67—68).—0·2 gram of iron or steel, or 0·1 gram of pig-iron, so finely pulverised that it passes through a 1·5 mm. sieve, is brought into the carefully dried reaction-tube of the apparatus. 4 c.c. of a saturated solution of cupric sulphate is added and allowed to react for 16 minutes, or, if a smell of hydrocarbon is detected, only three to four minutes. This reaction-tube is 140 mm. long, and 20 mm. wide, and is closed at the top by a doubly bored india-rubber stopper. Through one of the holes passes a funnel with stopcock; the other is connected with a burette. This has an india-rubber stopper at its upper end, through which passes a funnel with stopcock; the lower end is connected with a water-flask for regulating the pressure. The burette is surrounded by a tube, through which water may be passed for regulating the temperature. After the cupric sulphate has acted on the iron, 1·2 grams of chromic acid is added to the mixture, stirred up well with a glass rod, and allowed to react for three to 10 minutes. The tube and contents are next cooled, the burette is filled with water and connected with the reaction-tube, and 8 c.c. of pure sulphuric acid passed gradually into the latter by means of the funnel with stopcock.

The tube is warmed gently up to the boiling point for 10 minutes, then cooled down, and finally all air and carbonic anhydride expelled out of the reaction-tube into the burette by passing in water through the funnel. The volume of gas in the burette having been read off, aqueous potash is passed in through the funnel, the gas shaken with it, and, after adjusting the level of the water, the volume again read off, when from the difference between the two readings the percentage of carbon in the iron may be calculated. J. W. L.

Absorption of Carbonic Oxide by Cuprous Chloride Solutions. By T. LONATSCHEFFSKY-PETRUNIAKA (*J. Russ. Chem. Soc.*, 1888, **20**, 108—123).—The author has analysed mixtures of gases (especially wood-petroleum gas) containing carbonic oxide by Bunsen's method, that is, absorption of that constituent by cuprous chloride. Clay balls were soaked with a solution of cuprous chloride in hydrochloric acid and introduced into the gaseous mixture to be analysed, but constant results could not be obtained. It was shown that such balls, saturated with carbonic oxide, lose some of this gas in pure hydrogen, whereas incompletely saturated balls either lose none or absorb more carbonic oxide when introduced into mixtures of hydrogen with little or much carbonic oxide. It is shown in a series of tables that the phenomena of absorption depend on the partial pressure of carbonic oxide in mixtures with other gases. The author's results were obtained independently of Drehschmidt's. B. B.

Action of Sulphuric and Hydrochloric Acids on Wood-Petroleum Gas. By T. LONATSCHEFFSKY-PETRUNIAKA (*J. Russ. Chem. Soc.*, 1888, **20**, 123—124).—By passing the gas into a hydrochloric solution of cuprous chloride, a solid substance and a volatile liquid of an aromatic character, and containing chlorine, are formed. Dilute sulphuric acid gives nothing but resinous compounds. These facts are of importance in connection with gas analysis. B. B.

Precipitation of Barium Sulphate in the Presence of Bromine. By M. LUCION (*Chem. Zeit.*, **12**, 427) and G. TAUBER (*ibid.*, 477).—Both authors independently have observed that bromine does not interfere with the accurate precipitation of barium sulphate; and, therefore, when it has been used for oxidising sulphur compounds, the removal of any excess, as generally recommended, is superfluous. D. A. L.

Analysis of Lead Peroxide. By L. OPIFICIUS (*Chem. Zeit.*, **12**, 477).—For this purpose the peroxide or red lead may be readily dissolved without the application of heat by treatment with nitric acid, sp. gr. 1·20, and chemically pure copper. In the case of red lead, especially, this method is very useful in detecting admixtures, as adulterants are left that would be dissolved by treatment with hot solvents; these can, therefore, be readily detected and estimated; further, if it is desired to determine copper also, it is only necessary to use a weighed quantity of that metal in the first instance. D. A. L.

Electrolytic Estimation of Copper. By F. Rüdorff (*Ber.*, **21**, 3050—3051).—In estimating copper electrolytically, it is advantageous to mix the solution with 2 to 3 grams of potassium or ammonium nitrate, and then to add about 10 c.c. of ammonia for every 100 c.c. of the solution containing from 0·1—0·3 gram of copper. The condition of the precipitated metal is very satisfactory, and the strength of the current employed may vary within tolerably wide limits.

F. S. K.

Estimation of Manganese in Foods. By G. Stein (*Chem. Zeit.*, **12**, 446).—The ash is boiled with nitric and sulphuric acids and lead peroxide, the resulting permanganate being determined by titration. In this way, by using 5 grams of ash, American coffee beans gave 0·0279 per cent. of manganese in the ash.

D. A. L.

Estimation of Iron and Alumina in the Presence of Calcium and Phosphoric Acid. By G. Kennepohl (*Chem. Zeit.*, **12**, 923—924).—The unsatisfactory results obtained in the estimation of iron and alumina in natural and artificial phosphates led the author to investigate the methods employed. These are numerous, but may be classified under three heads: those depending on (1) the precipitation and estimation as double phosphate of iron and aluminium; (2) precipitation by means of ammonium acetate and estimation of the calcium and phosphoric acids; and (3) separation of iron and aluminium. The latter is much too tedious for general application, and numerous quantitative experiments with mixtures of solutions of ferric chloride, aluminium sulphate, and calcium phosphate, dissolved in nitric acid, in some cases with ammonium phosphate and calcium, in other cases without one or the other, or both, lead the author to conclude that methods 1 and 2 are far too inconvenient when accurate results are required, owing to the difficulty of separating calcium compounds and phosphoric acid. The following method is, therefore, recommended:—The solution is neutralised, or made slightly ammoniacal with ammonia, in a 100 or 200 c.c. flask; it is then treated with slight excess of oxalic acid, heated at 80° for some time, filled to the mark, and filtered. A measured quantity of the clear filtrate is evaporated to dryness, and gently ignited in a platinum dish. The residue is moistened with concentrated ammonia, dried, and dissolved in concentrated hydrochloric acid. The solution is precipitated by means of ammonia and acetic acid, the iron and alumina being weighed as double phosphate, in which the iron may, if desired, be estimated in the usual way. The method also serves for the estimation of calcium, and may be made volumetric by employing standard oxalic acid. Another method, in which phosphoric acid was first eliminated by magnesia mixture in the presence of citric acid, did not prove satisfactory.

D. A. L.

Separation of Nickel and Cobalt in the Form of Nitrites. By Baubigny (*Compt. rend.*, **107**, 685—686).—Lang showed that barium nitrite forms an insoluble triple compound with potassium and nickel nitrites, and thus prevents the accurate separation of nickel and cobalt by this method. The author finds that lead nitrite also forms an insoluble triple compound with the nickel and potassium, which separates as an orange-yellow precipitate only slightly soluble in acetic acid. The composition of the precipitate varies with the proportions of the three salts in the solution, but it is evident that it interferes with the separation of nickel from cobalt.

C. H. B.

Volumetric Estimation of Stannous Chloride. By A. JOLLES (*Chem. Zeit.*, **12**, 597).—The following method is found satisfactory for the estimation of stannous chloride:—4 or 5 grams of potassium manganate dissolved in 8 or 10 grams of potassium hydroxide, and made up to a litre, is standardised by means of potassium antimony tartrate. 0·2 or 0·4 gram of the stannous chloride, or metallic tin, is dissolved in hydrochloric acid in a current of carbonic anhydride, and made up to 250 c.c. This solution is then run from a burette into 5 or 10 c.c. of the manganate solution, until the green colour is replaced by a yellowish-brown, the volume is read off and calculated as usual; the reaction is represented by the equation:—$SnCl_2 + 2KOH + K_2MnO_4 = 2KCl + SnO_2 + 2KOH + MnO_2$. When the stannous chloride is much contaminated, it is advisable to precipitate the tin by means of zinc, and then proceed as above. D. A. L.

Estimation of Titanium and Phosphorus in Iron Ores. By JENNINGS (*Chem. Centr.*, 1888, 1234, from *Berg. Hütt. Zeit.*, **47**, 294). —1 to 5 grams of the ore is digested with hydrochloric acid, the solution neutralised with sodium carbonate, reduced with sulphurous acid, 50 c.c. of acetic acid added, and diluted to 500 c.c. By boiling for one hour, the titanic acid is precipitated, a part of the phosphoric acid and iron accompanying it. The precipitate, with the insoluble portion of the ore (the latter is purposely allowed to remain in the solution, as it assists in the filtration of the titanic acid), is brought on to a filter and washed with dilute acetic acid, dried, ignited, fused with 10 times its weight of sodium carbonate, and the silicate and phosphate of soda dissolved out of the flux. The insoluble sodium and iron titanate is dissolved in dilute sulphuric acid, neutralised with sodium carbonate, reduced with sulphurous acid, and the titanic acid precipitated pure with 25 c.c. acetic acid. The first two filtrates are mixed together, oxidised with nitric acid, and the phosphoric acid, as well as some silicic acid, precipitated with ammonia; the precipitate is dissolved and evaporated to dryness, in order to render the silicic acid insoluble, and the phosphoric acid determined with molybdate solution. J. W. L.

Estimation of Noble Metals in Potassium Cyanide Solutions containing them. By L. OPIFICIUS (*Chem. Zeit.*, **12**, 525). —The solution is treated with hydrochloric acid to destroy the cyanides, warmed, sulphuric acid added, and the gold and silver precipitated by means of zinc, their complete precipitation being indicated by the appearance of a deposit of metallic copper, which is generally present in such solutions. The metallic precipitate is washed, mixed with lead, cupelled, parted, &c., in the usual manner. The method is both rapid and accurate. D. A. L.

Modifications in the Methods of Organic Analysis. By W. L. Dudley (*Ber.*, **21**, 3172—3177).—The author recommends the employment of a platinum combustion-tube and manganese sesquioxide, instead of copper oxide, and states that with such an apparatus a combustion can be made every hour with very satisfactory results. In the analysis of volatile liquids, the substance is weighed in a small bulb-tube, the two ends of which are bent upwards. When the combustion-tube is sufficiently hot, the bulb is interposed between the drying apparatus and the tube, and a stream of nitrogen passed; as soon as the air in the combustion-tube is expelled, an iron plate placed a few inches underneath the bulb is heated, so that the liquid quickly volatilises into the combustion-tube without condensing in its passage there. When the liquid has all volatilised, air or oxygen is passed, and the process completed as usual. F. S. K.

Source of Error in the Estimation of Benzene in Coal-gas. By F. P. Treadwell and H. N. Stokes (*Ber.*, **21**, 3131—3133).—In Berthelot's method for the analysis of coal-gas, fuming nitric acid is used to absorb the benzene, and bromine-water to absorb the hydrocarbons C_nH_{2n} and C_nH_{2n-2}. It is shown by the author that fuming nitric acid absorbs carbonic oxide completely (compare Hasenbach, *J. pr. Chem.* [2], **50**, 1), and that bromine-water absorbs benzene, as well as the hydrocarbons mentioned (compare also Drehschmidt, *Post's Chem. Techn. Anal.*, 1888, 108). N. H. M.

The Amount and Estimation of Fusel Oil in Spirits. By F. L. Ekman (*Chem. Zeit.*, **12**, 564—565).—According to the results of the author's investigations, brandies prepared from potatoes or cereals, with the exception of normal propyl and isobutyl alcohols, contain no other alcohols with boiling points between ethyl and amyl alcohols; this is at variance with the statements of some previous observers. The fusel oils from such spirits contain from 3—12 per cent. by weight of propyl alcohol, 15—47 of butyl alcohol, 44—71 of amyl alcohol, with 5—7 per cent. of high-boiling residue. The largest proportion of butyl alcohol was found in spirit from cereals. The various constituents were separated by fractionation, using a Le Bel tube; the corn spirits required 20—25 fractionations to get the propyl alcohol sufficiently pure. The sp. grs. at 15° were propyl alcohol 0·8085, isobutyl alcohol 0·8064, amyl alcohol 0·8157. The amount of these oils was estimated colorimetrically by means of sulphuric acid. The types were strong solutions containing hydrochloric acid and known quantities of cobaltous chloride for red, ferric chloride for yellow, and copper chloride for blue. 200 c.c. of spirit and 25 c.c. of water are rapidly distilled from a brass retort until 185 c.c. have passed over. The distillate is diluted to 200 c.c., and 25 c.c. is steadily run into 15 c.c. of sulphuric acid, sp. gr. 1·8436, during about five minutes, with brisk stirring; they are compared with the types after a lapse of at least three hours. Propyl alcohol is not coloured by sulphuric acid. Aldehyde to the extent of 0·02 per cent. in 46 per cent. alcohol gives no noteworthy reaction with sulphuric acid, but, nevertheless, is objectionable, as it has the property of intensifying the colour reaction of amyl alcohol, and may lead to considerable error. D. A. L.

Estimation of Sugar in Molasses by Clerget's Inversion Method. By F. Herles (*Chem. Centr.*, 1888, 1136—1137, from *Zeit. Zuckerind Böhmen*, **12**, 381—387).—Owing to the presence of raffinose in molasses, the determination of the sugar is not made by directly polarising, but, according to Clerget's method, after inversion. As the raffinose is fermentable, the author considers that it should not be omitted from the percentage of sugar, and he proposes the following method and formula. The molasses is clarified with plumbic acetate in a 100 c.c. flask, 50 c.c. is inverted with 5 c.c. concentrated hydrochloric acid, by heating at 70° for 15 minutes. After cooling, the degree of rotation is noted as well as the temperature. Then the difference between the two readings of the polariscope, before and after inversion, is multiplied by 0·42, and added to the determination according to Clerget. For temperatures approaching 20°, the author recommends the calculation of the sugar contents from the reduction of the rotation (S) on account of inversion:—

$$C = \frac{100S}{142 - t/2}, \text{ where } t = {}^\circ\text{C}.$$

J. W. L.

Estimation of Saccharose as well as Invert-sugar or Raffinose and on the Quantitative Estimation of Glucose with Levulose. By J. Dammüller (*Chem. Centr.*, 1888, 1248, from *Zeit. Ver. Rüb. Zuck. Ind.*, **25**, 742—755).—The author prefers weighing half the normal weight of sugar for inversion (namely, 13·024 grams) dissolving in 75 c.c. of water and inverting with 5 c.c. of concentrated hydrochloric acid by heating at 70° for $7\frac{1}{2}$ minutes. The resulting solution is then diluted to 100 c.c. and polarised. Then, since 26·048 grams cane-sugar cause a deviation of +100°, and further, the same weight of cane-sugar after inversion causes a deviation of −32·66°, then for each +1° (=1 per cent.) rotation before inversion, the same amount of cane-sugar causes a rotation of −0·3266° after inversion. Under the same conditions of inversion, 16·576 grams of raffinose ($C_{18}H_{32}O_{16} + 5H_2O$), causes before inversion a rotation of +100°, after inversion of +51·82°; before inversion, therefore, it rotates the ray 1·852 times more strongly than cane-sugar. 26·048 grams of anhydrous raffinose, after inversion, would rotate the ray +95·98°. If now P = the reading in degrees of deviation caused by 26·048 grams sugar before inversion; J = the reading after inversion; Z = the percentage of cane-sugar; and R = the percentage of anhydrous raffinose;

then (1) $P = Z + 1{\cdot}85\,R.$
(2) $J = -0{\cdot}3266\,Z + 0{\cdot}9598\,R,$

from which we obtain—

$$Z = 0\cdot5188\,P - J/0\cdot8454 = \text{per cent. cane-sugar},$$
$$R = P - Z/1\cdot85 = \text{per cent. raffinose.}$$

The author has experimented with Sieben's method for destroying levulose, but the results obtained were not altogether satisfactory, especially when the proportions of levulose and glucose varied.

J. W. L.

Estimation of Raffinose in Beet-sugar. By G. LOTMAN (*Chem. Zeit.*, **12**, 391—392).—Simple examination of the methyl alcohol extract of sugar gives too high a percentage of raffinose. The following method gives accurate results with even 0·1 per cent. of raffinose. 50 grams of the sugar is perfectly dried at 60° with the aid of a water-air-pump, allowed to cool in the drying chamber, and treated with 100 c.c. of methyl alcohol and polarised. 50 c.c. of the solution is then mixed with 2 c.c. of a solution of lead acetate (sp. gr. 1·4, which precipitates all the raffinose), made up to 55 c.c., and again polarised. This reading +10 per cent. gives the rotation due to cane-sugar, and by deduction from the first reading, the rotation due to raffinose is found, and the percentage calculated as usual. One part of raffinose prevents the crystallisation of at least five parts of sugar.

D. A. L.

Detection of Foreign Starches in Chocolate. By C. HARTWICH (*Chem. Zeit.*, **12**, 375).—Owing to the variable amount of starch in cocoa-beans, chemical examination of chocolate cannot be taken as decisive, as regards admixture of foreign starches, unless the percentage is above 10 per cent. Therefore, microscopical examination is resorted to, and for this purpose the chocolate is best deprived of its fat and sugar before being placed under the microscope. The starch granules are counted in different parts of the object, and a mean taken; a pure chocolate is then mixed with a corresponding amount of the supposed foreign starch, and examined in the same manner; in this way, the quantity of starch may be estimated with sufficient accuracy.

When small-grained starches are present, it is not advisable to treat with iodine in potassium iodide beforehand. D. A. L.

Butter Analysis. By PAGNOUL and GRENET (*J. Pharm.* [5], **18**, 353—360).—The present rapid method of analysis is based on a determination of both the volatile and fixed acids in the butter. 10 grams of butter is just melted and transferred to a burette graduated to 70 c.c., into which a few drops of warm water and a little light petroleum have been previously placed. The capsule in which the butter has been melted is washed alternately with petroleum and a few drops of water, and the burette is filled up with petroleum to a point below the 70 c.c. mark. The burette is closed above with the moistened hand, and strongly shaken, after which it is allowed to remain five or six minutes. Then the water level is brought up to 10 c.c., and the petroleum level up to 70 c.c., and after shaking again the tube is closed and allowed to remain for 10 minutes. If the temperature is low, it may be necessary to warm the burette a little. The aqueous portion is carefully drawn off into a tared platinum dish, a little water being added several times, to remove all that is soluble in water. This solution serves to determine the foreign matters—ash and sodium chloride. 10 c.c. is now run out of the burette and thrown away, then 20 c.c. is run into a flask for the estimation of the fatty acids, and 20 c.c. more is run into a tared capsule for estimation of the total fat. The flask just mentioned is heated on the water-bath for 5 to 10 minutes to expel the petroleum; then for saponification there is added 50 c.c. of a solution prepared as follows:—60 grams of potash-lime is placed in a flask with 800 c.c. of alcohol of 95°, and agitated from time to time during several days; this is then filtered and made up to a litre. The flask containing the fatty matter and alkaline solution is heated at 100° and agitated from time to time, but more actively towards the end of the operation; in 30 to 40 minutes the saponification is complete. 50 c.c. of water is now added, and warmed a little to dissolve the soap, three or four bits of pumice and 12 c.c. of phosphoric acid of 45° are then added. The flask is shaken and closed with a stopper carrying a funnel with stopcock and a tube with two bulbs in the vertical portion and then bent slightly downwards and leading to a vertical worm condenser. When 45 c.c. has been distilled over, 50 c.c. of water is passed into the flask; when 95 c.c. has passed over, a second 50 c.c. of water is added, and the distillation is continued until 145 c.c. has passed over. Phenolphthaleïn is added to the distillate and decinormal soda solution. The volatile fatty acids expressed as butyric acid, per 100 of butter, equals 0·264 time the number of c.c. of soda solution used. With margarin, only 1 or 2 c.c. is required, whilst pure butter requires about 20 c.c. The presence of sodium chloride in the flask would give rise to hydrochloric acid, which would be estimated as so much fatty acid. If present, the titrated liquid may be acidified with a few drops of nitric acid, and neutralised with calcium carbonate in excess, then potassium chromate and standard silver nitrate solution will indicate the amount of hydrochloric acid which is to be deducted. 20 to 25 c.c. of light petroleum is added to the warm residue in the flask, and the contents are transferred to the burette, the flask is then washed alternately with petroleum and warm water to collect the whole of the residue. On running off the water from the burette, the phosphoric acid and glycerol are removed; three or four washings give a water which is quite neutral. The solution of fatty acids thus completely washed is evaporated on the water-bath, the capsule being sunk in the boiling water, so that the outside level is 2 or 3 cm. higher than that of the inside; the residue is dried at 105° or 110°, and weighed. The platinum capsule containing the other 20 c.c. of petroleum solution is evaporated, dried at 105° to 110°, and weighed. From these figures the amount of fixed and volatile fatty acids per cent. of fatty matter are deduced. The platinum capsule containing the original 10 c.c. of aqueous solution is evaporated, dried, and weighed; then gently heated to dull redness and weighed again. The ash is dissolved in a little water, filtered, and the liquid is made up to

100 c.c. In 20 c.c., the chlorine is titrated with silver nitrate solution and potassium chromate. Finally, the moisture is determined on 5 grams of butter mixed with 8 or 10 little balls of paper, made from one of two dried and balanced filters. By turning over the paper balls two or three times, the drying is completed at 105° to 110° in about three hours. If boric or salicylic acid is suspected, special methods then become necessary. J. T.

Detection of Cotton-seed Oil in Lard. By W. Bishop and L. Ingé (*J. Pharm.* [5], 18, 348—353).—American lard imported into France is frequently adulterated with 50 to 60 per cent. of other fats; cotton-seed oil is often used, and the desired consistence is given to the mixture by the addition of pressed tallow. Bechi has shown that cotton-seed oil, to the exclusion of other fats, reduces silver nitrate. (Compare, however, Bizio, this vol., p. 86.) Labiche has remarked the production of a special coloration when this oil is treated with lead acetate and ammonia. Finally, the rise in temperature produced by mixing this oil with sulphuric acid is relatively considerable. These three characteristics are sufficient to detect the oil, when mixed with lard, as follows:—100 to 150 grams of the lard is heated at 80—100° until it becomes perfectly clear. 5 grams of this limpid material is treated with 20 c.c. of absolute alcohol and 3 c.c. of a solution containing 2 grams of silver nitrate to 250 c.c. of absolute alcohol. The mixture is heated at 100° during 10 minutes, and stirred from time to time. In presence of cotton-seed oil, a more or less accentuated coloration is produced, and a coloured cake is formed on cooling; on decanting the alcohol and dissolving the cake in ether or light petroleum, a cold solution is obtained, having the same colour. Again, 25 grams of the limpid fat is treated with 25 c.c. of a solution, cooled to about 35°, made up of crystallised lead acetate 500 grams, and water 1000 c.c., 5 c.c. of pure ammonia of 22° B. is then added, and the mixture is vigorously stirred for some minutes to form a homogeneous emulsion. After 24 hours the colour is observed. Finally, 25 grams of the melted fat is cooled to about 30°, the temperature is taken, and 20 grams of sulphuric acid, of sp. gr. at least 1·836, is added. The mass is strongly agitated, and the point of maximum temperature observed. By operating always in the same way, duplicate experiments will give readings not differing by more than two degrees. Comparative experiments are made at the same time with pure materials. The authors have not succeeded in devising a quantitative method.

J. T.

Estimation of Fatty Acids in Soap. By Samelson (*Chem. Zeit.*, 12, 355).—The fatty acids are precipitated by means of sulphuric acid, and are collected and washed on a tared filter. The filter and precipitates are then transferred to a weighed weighing bottle, treated first with absolute alcohol, which is driven off on a water-bath, then with ether in a similar manner. After this treatment, the tube and contents are placed in a water-oven, and are dry in an hour. The method is speedy, and avoids both loss and decomposition of the fatty acids. D. A. L.

Detection and Estimation of Salicylic Acid, chiefly in Beer. By H. Elion (*Rec. Trav. Chim.*, **7**, 211—219).—The acid is extracted from the solution containing it, by shaking it with two or three times its volume of ether; the ethereal solution, after separation, is then shaken up with a small quantity of a dilute solution of soda or potash, which takes up the whole of the acid. In a very small portion of the solution, after acidification with hydrochloric acid, the salicylic acid can usually be detected by means of the ferric chloride test.

If the acid is extracted as above from beer, the impurities which accompany it prevent its direct estimation by evaporating the ethereal solution and weighing the residue. Direct titration by means of dilute alkali also gives unsatisfactory results. Excess of bromine converts salicylic acid into the compound $C_6H_2Br_3{\cdot}OBr$, and this, by the action of potassium iodide, is converted into potassium tribromophenoxide, $C_6H_2Br_3{\cdot}OBr + 2KI = C_6H_2Br_3{\cdot}OK + I_2 + KBr$. The author attempted, by determining the iodine liberated in the latter reaction, to estimate the salicylic acid by this means, but found that the action of the potassium iodide was far from complete at the ordinary temperature and with moderately dilute solutions. Estimation of the hydrobromic acid formed when salicylic acid is converted into tribromophenol by excess of bromine, also gave discordant results in the case of beer, owing to the presence of foreign organic matter. It was finally decided to determine the salicylic acid by separating and weighing the tribromophenol itself. This can be done by steam distilling the solution, after removing the excess of bromine by means of potassium iodide and sodium thiosulphate, extracting the distillate with ether, and evaporating the ethereal solution. This last method was found to yield satisfactory results. H. C.

Detection of Salicylic Acid in Beer. By A. J. C. Snyders (*Chem. Centr.*, 1888, 1186, from *Rev. internat. fabricat. aliment*, **1**, 166—170).—25 c.c. of beer, with a few drops of sulphuric acid, is shaken up with 40 c.c. of ether, and the ether extract is tested with very dilute ferric chloride. By this means, 0·004 gram of salicylic acid per litre of beer may be detected. For the quantitative estimation, 250 c.c. is distilled and the first 130 c.c. of the distillate is taken.

J. W. L.

The Simand-Kohnstein Method of Estimating the Acids in Tanning Liquors. By R. Koch (*Dingl. polyt. J.*, **269**, 168—182).—In a recent communication (*Gerber*, **323** and **324**), Simand, in defending the gravimetric method of estimating the free acid in tannins (Abstr., 1885, 935), refers to the author's criticisms, and asserts that Koch wrongly condemns the method owing to the fact that, through the formation of sparingly soluble magnesium salts, a considerable error arises in the estimation of free acids by the Simand-Kohnstein method.

The author in reply states, that although, from a scientific point of view, he quite agrees with this contention, having recently carried out a further series of experiments to prove the correctness of the supposed formation of sparingly soluble magnesium salts, he condemned the method as being useless for practical purposes on account of its extreme tediousness and complexity, and, therefore, advocates the estimation of the free acids in tanning liquors by his titration method. (Compare Abstrs., 1887, 871, 1144; and 1888, 1138.) D. B.

Testing Peru Balsam. By C. DENNER (*J. Pharm.* [5], **18**, 259—260, from *Gehe's Handelsber.*, 1888).—To detect gum benzoïn or storax in Peru balsam, 5 grams of the balsam is treated with 5 grams of sodium hydroxide solution (Ph. Germ., II) and 10 grams of water. The whole is well shaken twice with 15 grams of ether, each time decanting the ether layers as completely as possible. The residue is boiled, and acidified with hydrochloric acid; on adding cold water, a resin separates which is dissolved in sodium hydroxide solution. The solution thus obtained is diluted with 20 grams of water, boiled, and precipitated with barium chloride; the precipitate thus formed is collected on a filter, dried on the water-bath, and extracted with alcohol. The residue is treated with concentrated sulphuric acid, and the liquid stirred up with chloroform. The chloroform becomes violet or blue if gum benzoïn or storax is present. This method is capable of detecting the presence of minute quantities. J. T.

General and Physical Chemistry.

Refractive Indices of Turbid Media. By A. Haschek (*Monatsh.*, 9, 900—902).—Solutions were made in alcohol of shellac, mastic and guaiacum, 8·9, 10·01, and 12·83 grams of each being taken to 100 grams of alcohol. 20 grams of each solution was added to 100 grams of water, and the refractive index then measured. These were for the sodium and lithium lines, mastic 1·3454 and 1·3341, guaiacum 1·3429 and 1·3401, shellac 1·3461 and 1·3410. A solution of water and alcohol alone, in the proportions in which each was present in the above liquids, gave 1·3365 and 1 3341.

Nine square centimetres of filter-paper were boiled in 100 c.c. sulphuric acid for half an hour, and the refractive index of the solution found to be 1·4320 and 1·4313, that of the acid alone being 1·4317 and 1·4310. On again boiling for half an hour the solution gave 1·4328 and 1·4320, and the acid 1·4318 and 1·4311.

Since in each solution there has been an increase in the refractive index, due to the suspended particles, it must be assumed that these particles cause a retardation in the velocity of light, the more so as this retardation appears to increase as the size of the particles decreases. H. C.

Refraction of Liquids within wide Limits of Temperature. By E. Ketteler (*Ann. Phys. Chem.* [2], **35**, 662—699).—In former papers (Abstr., 1888, 541), the author established, in the case of water and alcohol, the two formulæ $(n^2 - 1)(v - \beta) = \text{M}$, and $\text{M} = \text{C}(1 + ae^{-kt})$. Of the four constants, β, C, a, k, occurring in these formulæ, β, a, and k have to be determined by refraction observations, whilst C may be assumed to be known independently.

In the present paper, the author describes an elaborate series of experiments on the refraction of carbon bisulphide, from the results of which he deduces the following conclusions:—

(1.) The coefficient β can be determined most accurately from the results of Zehnder's and Quincke's pressure researches.

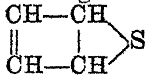
(2.) The refraction of carbon bisulphide within the limits of temperature of the observations $-20°$ to $160°$, is approximately given by the formula $(n^2 - 1)(v - \beta) = \text{constant}$.

(3.) The dispersion, given by the expression $(n^2_a - 1)/(n^2_0 - 1) - 1$, diminishes with the density, the decrease being such as would be accounted for by a change in the maximum absorption, proportional to the change of density.

(4.) Assuming these relations, the temperature-coefficient can be determined for all temperatures and wave-lengths.

Tables are given showing the indices of refraction for wave-lengths corresponding with the lines A, C, D, F, G, and H of the solar spectrum for different temperatures, with the corresponding values of the temperature-coefficient, and the incorrectness of the principal older formulæ. G. W. T.

Molecular Refraction of Fumaric, Maleïc, Mesaconic, Citraconic, and Itaconic Acids, and of Thiophen. By C. Knops (*Annalen*, **248**, 175—231).—The author has determined the index of refraction of the methyl, ethyl, and propyl salts of fumaric, maleïc, mesaconic, citraconic, and itaconic acids. A comparison of the molecular refraction of these acids and their ethereal salts, leads the author to the conclusion that fumaric and maleïc acids contain only one double-linked carbon-atom, and that fumaric acid stands in the same relation to maleïc acid that mesaconic acid does to citraconic acid (Abstr., 1888, 938). Brühl's theory is at present incapable of indicating in what points the constitution of fumaric and mesaconic acids differ respectively from the isomeric maleïc and citraconic acids. According to Anschütz (Abstr., 1887, 916; 1888, 448), ethyl fumarate and mesaconate contain two double-linked oxygen-atoms, but the isomeric maleate and citraconate only contain one double-linked oxygen-atom.

The molecular refraction of thiophen indicates that this compound contains only one double-linked carbon-atom. Further investigation is required in order to decide whether the formula  correctly represents the constitution of thiophen. W. C. W.

Preparation of Phosphorescent Calcium and Strontium Sulphides. By E. Becquerel (*Compt. rend.*, **107**, 892—894).—When calcium carbonate, as pure as possible, is calcined with sulphur, it yields calcium sulphide which is only feebly phosphorescent. If, however, traces of a sodium compound are added before calcination, the product shows a brilliant and persistent green phosphorescence. Manganese or bismuth alone has very little influence on the result, but in presence of traces of sodium, the former produces a brilliant yellow and the latter a brilliant blue phosphorescence. Lithium is even more active than sodium, and the phosphorescence is green. Potassium, on the contrary, has very little effect. From these results, it follows that the simultaneous presence of an alkali is essential to the production of any phosphorescence by manganese or bismuth.

Oyster shells and other shells, and aragonite and gypsum from some localities, contain sodium, and hence the phosphorescent properties of the calcium sulphide prepared from these substances.

If 0·1 part of rubidium carbonate is added to calcium carbonate which also contains a small quantity of sodium, and the mixture is heated with sulphur to a moderate temperature, the middle of the mass has a red colour, whilst the outer parts in contact with the crucible show a green phosphorescence. When the product is recalcined, the red disappears and only the green remains.

Strontium sulphide shows similar phenomena, which, however, are less strongly marked; if free from sodium, it shows a feeble, greenish-blue phosphorescence. In presence of lithium, the phosphorescence is yellow. With rubidium, no red colour is observed. Pure strontium oxide and pure sulphur yield a sulphide with a violet-blue phosphorescence, which, in presence of sodium or lithium, becomes greenish or yellowish in parts. C. H. B.

Decomposition of the Haloïd Salts of Silver by the Action of Light. By F. GRIVEAUX (*Compt. rend.*, **107**, 837—839).—The author's experiments lead him to the conclusion that the decomposition of the haloïd salts of silver by the action of light is a phenomenon of dissociation similar to the decomposition of the same compounds when heated. This view is supported by the following phenomena which are especially well marked in the case of silver iodide. When a beam of light is allowed to fall on one of two silver plates coated with silver iodide and immersed in a cell filled with liquid, an electromotive force is developed, and attains a maximum after a certain time. If iodine solutions of different concentrations are allowed to circulate in the cell, the plates coated with silver iodide remaining the same, the electromotive force diminishes as the concentration of the iodine increases, and at a particular concentration it becomes *nil.* If the distance between the cell and the source of light is gradually increased, the concentration of the iodine solution required to produce zero E.M.F. gradually diminishes, and *vice versâ.* If the cell is gradually moved to or from the light, and finally placed at a distance *d*, the E.M.F. developed is the same as if the cell had been placed at *d* at the beginning. When the concentration of the iodine solution in the cell gradually varies, the E.M.F. also varies gradually, but in the inverse direction. If when the E.M.F. has reached its maximum value the circulation of the iodine solution is stopped, the E.M.F. increases gradually and regularly, but when the circulation is restored the E.M.F. gradually sinks to its normal value for the particular degree of concentration. This result may be ascribed to the decrease in the concentration of the solution, due to the action of the iodine on water under the influence of light, a decomposition which is rendered evident by the decolorisation of the solution.

Similar phenomena are observed with silver bromide and silver chloride, but the concentration of the solution required to produce zero E.M.F. varies with the nature of the haloïd. C. H. B.

Decoloration and Recoloration of Litmus Solution by Light. By F. BELLAMY (*J. Pharm.* [5], **18**, 433—435).—That litmus solution loses its colour when kept in a closed vessel, and regains it on exposure to air, is well known. The author boiled 50 grams of litmus three times with three successive litres of water. Four flasks were filled with the last solution and hermetically sealed, so as to include only a small bubble of air. The flasks were placed on a table near to a window where, as a rule, only diffused light fell on them. Between August 24 and October 2 the four liquids became quite colourless. On October 15, one of the flasks had become somewhat coloured, and this grew in intensity until November 12, when it had reached its original intensity; the other three remained colourless. The coloured flask, placed alternately in darkness and light, became colourless, and coloured four and three times respectively, finally the flask was broken by expansion of the liquid caused by the direct action of sunlight.

The author has only been able to repeat the experiment once, and that less satisfactorily; he has not yet made out the cause of the changes of colour, but is working at the question. J. T.

Minimum-point of Change of Potential of a Voltaic Couple. By G. GORE (*Proc. Roy. Soc.*, **44**, 294—296).—The effect of dissolved substances on the electromotive force of a magnesium-platinum couple in distilled water (this vol., p. 90) can be easily shown by balancing one couple against another through a galvanometer, the salts experimented with being added to one of the couples. The plates must be cut from the same piece of metal, and immersed at the same time in separate quantities of the same water. The results are compared with those obtained by means of a thermopile. The minimum-point of change depends on the couple and liquid used, temperature, and particular galvanometer. The latter effect is probably dependent on the inertia of the needle. The minimum-point is dependent on the free chemical energy, and, with certain exceptions, on the chemical heat of the substance dissolved. H. K. T.

Change of Potential of a Voltaic Couple. By G. GORE (*Proc. Roy. Soc.*, **44**, 296—300).—The effect of potassium chlorate and chloride, hydrochloric acid, and bromine at different temperatures in increasing the voltaic potential of a zinc-platinum couple is examined (see preceding Abstract). The electromotive force increases more or less regularly with increase of the strength of the solution; in some cases (potassium chlorate and chloride) it reaches a maximum before the saturation point is reached; in others (potassium chloride and bromine) a momentary decrease is observed; in others the electromotive force becomes constant for a time, and then again increases. The amount of salt required for minimum change is greatest with potassium chlorate, least with bromine. The total increase in electromotive force is given. H. K. T.

Influence of the Chemical Energy of Electrolytes on the Minimum-point and Change of Potential of a Voltaic Couple. By G. GORE (*Proc. Roy. Soc.*, **44**, 300—308).—A continuation of experiments on the "minimum-point" (see preceding Abstracts). The quantities of dissolved salt required for the minimum-point of change for the oxyhalogen salts of potassium are in the order chlorate, bromate, iodate, beginning with the greatest; hence the more feebly united the negative constituent, the smaller the proportion of salt required to disturb the voltaic balance. With the haloïd salts, the minimum quantity was much smaller and in the order iodide, bromide, chloride; hence the action is more powerful, and the order of activity reversed. With the halogens themselves, the quantity required is still less, the order remaining the same; hence the effect is greater the greater the chemical energy of the substance and the greater the freedom of that energy. At low potentials the rate of increase of the electromotive force per unit weight of substance is larger the greater the effect of the substance. The curve of variation of potential is characteristic for each substance. H. K. T.

Effects of different Positive Metals on the Change of Potential of a Voltaic Couple. By G. GORE (*Proc. Roy. Soc.*, **44**, 368—377).—A continuation of the above experiments, in which the metals and form of galvanometer are varied. The more easily the positive plate, or the less easily the negative plate is corroded, the smaller the quantity of dissolved substance required to disturb the balance. With chlorine and bromine, the quantities vary directly as the atomic weights of the positive metals in the couples magnesium-platinum, zinc-platinum, cadmium-platinum. As the smallness of the quantity of substance required to disturb the balance depends both on the sensitiveness of the galvanometer and on the chemical energy of the substance, it is probable that the effect really begins with the first addition of substance, but is too small to detect. H. K. T.

Certain Generic Electrical Relations of the Alloys of Platinum. By C. BARUS (*Amer. J. Sci.*, **36**, 427—442).—Measurements of the conductivity of a large number of alloys of platinum with other metals are given, and also the observed temperature-coefficient for each alloy. Plotting the temperature-coefficients against the specific resistance, it appears that the effect of alloying platinum with less than 10 per cent. of any other metal is to produce a variation in the temperature-coefficient which is quite independent of the special ingredients, and depends only on the resistance of the alloy. Also, although the resistance of the alloys examined varied from 10 to 65 microhms. per c.c., throughout the whole of this enormous variation the temperature-coefficient was found to vary as a linear function of the conductivity. The author shows that a similar relation holds good in the case of alloys of other metals. H. C.

Electrical Resistance of Mercury. By F. KOHLRAUSCH (*Ann. Phys. Chem.* [2], **35**, 700—764).—This paper contains a very full account of a determination of the absolute resistance of mercury carried out by Weber's method of damping with some modifications of Dorn's. The result of the determination gives 94060 centimetre-seconds as the resistance of a cubic centimetre of mercury at 0°. Glazebrook has compared one of the author's mercury standards with the B.A. unit in the Cavendish Laboratory, and the result of the comparison gives one B.A. unit = 0·9866 ohm.

It will be remembered that at the Paris Conference it was determined that the legal ohm should be the resistance of a column of mercury 1 square centimetre in sectional area, and 106 centimetres in length at 0°. It was considered practically certain at the time that this length was a little too short, but as the amount of the excess was doubtful it was considered advisable to adopt the whole number. According to the author the true value lies between 106·2 and 106·3 centimetres. G. W. T.

Influence of the State of Aggregation of various Substances on their Electrical Resistance. By L. GRUNMACH (*Ann. Phys. Chem.* [2], **35**, 764—772).—Clausius has pointed out (*Ann. Phys. Chem.*, **104**, 650) that from Arndtsen's researches on the electrical resistance of metals, it follows that in the case of simple metals in the solid state, the resistance varies directly as the absolute temperature. Werner Siemens (*ibid.*, **113**, 91) has confirmed this conclusion, subject to the condition that it only holds when the metal is not near the melting point.

In the present paper, the author describes some observations of the resistance of mercury at temperatures ranging from −90° to + 20°. He obtains the value 0·00086 for the temperature-coefficient of liquid mercury, which agrees fairly well on the one hand with the value 0·00095 given by Werner Siemens, and on the other hand with the value 0·000882 given by Mascart, Nerville, and Benoît. During liquefaction he finds that the resistance undergoes a rapid increase up to about 1·5 times its original value, a much smaller increase than that given by Cailletet and Bouty, and by C. L. Weber. He finds, moreover, that the temperature-coefficient does not remain constant between the temperatures −40° and −90°, but steadily diminishes with the temperature, as shown briefly in the table below:—

Temperature.	Temperature-coefficient.
−40° to −50°	0·00226
−50 „ −60	0·00134
−60 „ −70	0·00111
−70 „ −80	0·00078
−80 „ −90	0·00037

These results show that pure mercury, with regard to its resistance, behaves differently from other simple metals, not only in the liquid state but even when solid, and at temperatures much below the melting point. G. W. T.

Electromotive Force of Selenium. By W. v. Uljanin (*Ann. Phys. Chem.* [2], **35**, 836).—Kalischer (this vol., p. 3) laid claim to a prior use of the method of preparing sensitive selenium at a temperature of 195°. While quite willing to grant this, the author points out that in his paper (Abstr., 1883, 883) he had expressly stated that the method he had employed was that originally described by Siemens in 1877, which he had found much better than the one claimed by Kalischer. The writer quite agrees with Kalischer that Fritts's results have nothing to do with the E.M.F. of selenium.

G. W. T.

Theory of the Dissociation of Electrolytes. By J. H. van't Hoff and L. T. Reicher (*Zeit. physikal. Chem.*, **2**, 777—781).—The relation which Ostwald has deduced (Abstr., 1887, 1020, 1142) as expressing the behaviour of electrolytes on dilution, $m^2/(1-m)v = C$, has been tested with a number of acids, and found to hold good with remarkable accuracy. The acids examined were acetic, butyric, benzoic, formic, and chloracetic. H. C.

Electrochemical Studies. By W. Ostwald (*Zeit. physikal. Chem.*, **2**, 840—851).—The conductivity of electrolytes may according to Kohlrausch be represented by $\mu = a + s$, where a and s are the ionic velocities, but since in electrolysis only the dissociated portion of the electrolyte is active, the proportion K of the electrolyte in the dissociated condition must be taken into account, and we get $\mu = K(u + v)$. Since u/v is known from Hittorf's measurements, and μ may be observed with certain salts at maximum dilution, we have all the elements for calculating the values of u and v.

The calculation of the velocities of a number of negative ions from observations of their sodium salts shows that for these velocities certain definite relations exist. Isomeric ions have the same velocity within very narrow limits. The examination of homologous series of acids shows very distinctly that as the number of atoms in the ion increases its velocity decreases. The nature of the elements of which the ions are composed influences the velocity, but this is more marked in the case of simple than in that of complex ions. Thus the difference between acetic acid and each of its chlorinated derivatives is very marked, whereas between benzoic and chloro- or bromo-benzoic acids it is hardly perceptible.

If the number of atoms in the anion is greater than 12, the velocity depends almost solely on this number, the differences, as before observed, being smaller and smaller the greater this number is. Hence if the number of atoms, as abscissæ, be plotted against the velocities as ordinates, a curve is obtained having its convex side towards the axis of abscissæ, which it approaches asymptotically, from which the velocity of any ion containing more than 12 atoms may be read off with an error of not more than 1 to 2 units.

H. C.

Specific Heat of Tellurium. By FABRE (*Ann. Chim. Phys.* [6], **14**, 101—103. Compare Regnault, *Ann. Chim. Phys.* [3], **46**, 280).—The specific heat of a sample of tellurium, precipitated by sulphurous acid, washed with water saturated with nitrogen, and dried in a stream of this gas, was found to be 0·05243 as the average of three experiments at temperatures ranging from 98·01° to 98·39°. The specific heat of the same sample, after having been distilled in a stream of sulphurous anhydride, was found to be 0·05177 as the average of three experiments at 97·62°, 97·7°, and 97·9° respectively. The element as thus obtained differed in appearance from tellurium which has been distilled in hydrogen, and it did not clearly show a crystalline fracture. Crystalline tellurium, prepared by decomposing alkaline tellurides, was washed with water saturated with nitrogen, distilled in an atmosphere of hydrogen, and then melted and cooled very slowly. Its specific heat was found to be 0·048265 as a mean of two experiments at 98·22° and 98·13°.

F. S. K.

Estimation of the Value of a Degree in Thermometers of Short Range. By L. CALDERON (*Ber.*, **21**, 3303—3315).—The method described below was employed for ascertaining very accurately the value of the graduations of a thermometer of short range by direct comparison with a standard thermometer. It is also suitable for determining the exact value of the graduations of thermometers, endiometers, &c., or for accurately measuring the height of the barometer, coefficients of expansion, &c.

If the distance a between two consecutive graduations n^1 and n^2 of a thermometer, between which the end of the mercury column stands, is measured in units sufficiently small, and if the distance p between the lower graduation n^1 and the end of the mercury column is also ascertained, the quotient p/a gives the fraction of the interval a occupied by the column of mercury. If q is the distance between the higher graduation n^2 and the end of the column of mercury, then $q = a - p$, and whatever the value of a, $p + q = a$. The two expressions p/a and q/a, either of which can be employed to control the other, will then give the distances of the mercury column from the two consecutive graduations n^1 and n^2 respectively in fractions of the unit employed.

The instrument employed for making the necessary measurements is a sort of cathetometer, a full description of which is given with the aid of a diagram. The author also describes in detail the *modus operandi*, and gives examples showing with what accuracy the graduations can be controlled. In one experiment with a standard thermometer registering from —0·5° to 100·5°, and divided into tenths of a degree, the distance between the graduations corresponding with 97·8° and 97·9°, was equal to 96 divisions on the micrometer scale of the cathetometer. The thermometer being placed in the vapour of boiling water, the distance from the end of the mercury column to the graduation 97·8° was 75 divisions on the scale; the exact temperature shown by the thermometer was therefore 97·87812°. In a second experiment, the thermometer being placed in melting ice, the distance between 0° and —0·1° was 102 divisions, and that between the end of the column of mercury and the zero point 28 divisions; so that the exact temperature registered was —0·02745°. The value of 1° of this thermometer, all corrections having been made, is therefore 0·999644°. The following day a change of more than 6 mm. having taken place in the height of the barometer, the temperatures registered by the same thermometer under the same conditions were 98·1632° and 0·06061°. The value of 1° after making all necessary corrections was therefore 0·999635°. A series of 16 observations was made in which the thermometer referred to above was compared with an instrument graduated from —0·3° to 14°, and divided into fifteenths of a degree; the mean error of observation was only ±0·004°. F. S. K.

Dilatation of Salt Solutions by Heat. By N. TSCHERNAY (*J. Russ. Chem. Soc.*, 1888, **20**, 430—442).—The author has determined the dilatation of several salt solutions by Marignac's method, using dilatometers the constants of which had been accurately determined previously. The following nitrates were investigated, V_t being volume at t° :—

(1.) $HNO_3 + 50H_2O$ $Vt = 1 + 0{\cdot}0001595t + 0{\cdot}000003699t^2$.
(2.) $LiNO_3 + 50H_2O$ $1 + 0{\cdot}0001471t + 0{\cdot}000003673t^2$.
(3.) $NaNO_3 + 50H_2O$ $1 + 0{\cdot}0002144t + 0{\cdot}000003194t^2$.
(4.) $KNO_3 + 50H_2O$ $1 + 0{\cdot}0001746t + 0{\cdot}000003575t^2$.
(5.) $AgNO_3 + 50H_2O$ $1 + 0{\cdot}0001593t + 0{\cdot}000003587t^2$.
(6.) $Ca(NO_3)_2 + 50H_2O$ $1 + 0{\cdot}0001719t + 0{\cdot}000003531t^2$.

He gives also the coefficients of dilatation dv/dt, the equations for the change of molecular volume with the temperature and the corresponding dilatation coefficients, &c. From a comparison of the different values, it is seen that the above solutions of nitrates have approximately the same dilatation coefficient at temperatures higher than 30°. The dilatation coefficients of molecular volumes are found not to agree when the temperature rises to 50°, and the difference between the numbers corresponding with different salts diminishes very slowly with falling temperature. B. B.

Table of Vapour-tensions of Solutions of Potassium Hydroxide. By G. ERRERA (*Gazzetta*, **18**, 225—231).—This is an elaborate table of vapour-tensions of solutions of potassium hydroxide of various strengths, containing from 1 to 49 parts of the hydroxide to 100 of water. It is an extension of Wüllner's table (*Ann. Phys. Chem.*, **110**, 564) in which the values for the various lacunæ in it are calculated and inserted: the formulæ used for temperatures below 52·84° being $D = 0·003320T - 0·00000432T^2$, and for 52·84° to 100° $D = 0·002863$; in which D indicates the diminution of tension produced by 1 part of the hydrate $KHO,2H_2O$ dissolved in 100 of water, and T the tension of water-vapour at the given temperature.

C. E. G.

Dissociation of Carbonic Anhydride. By H. LE CHATELIER (*Zeit. physikal. Chem.* **2**, 782—786).—The author shows that by aid of the formula $\log P + \log \frac{x^3}{(2+x)(1-x)^2} - 500 \int \frac{2L}{T^2}\, dT = \text{const.}$, the dissociation coefficient x of carbonic anhydride at the temperature T and pressure P may be calculated, L being the molecular heat of formation of carbonic anhydride. The results agree very well with the experiments of the author, Mallard, Crafts, and Deville.

The value of L decreases with rising temperature, and at length becomes equal to zero, when the dissociation coefficient reaches a maximum. This maximum will be smaller the greater the pressure, a result which is in contradiction to the ordinary idea that at a sufficiently high temperature all substances undergo complete dissociation.

H. C.

Rise of Salt Solutions in Capillary Tubes. By M. GOLDSTEIN (*J. Russ. Chem. Soc.*, 1888, **20**, 408—415).—The author has found, as Valson did, that the heights of liquids in capillary tubes are inversely proportional to their densities, so that hd = const. This rule, however, holds good only in the case of very dilute solutions, the value hd growing with increasing concentration. In such a case, the capillary rise of the solution is found to be a function not only of the density, but also of the molecular weight of the salt dissolved. In concentrated solutions containing one and the same percentage of different salts, the height of the column increases with a decreasing molecular weight of the salt dissolved. Inversely, when two different solutions give columns of the same height, that salt, which is in smaller quantity, is sure to have a larger atomic weight. The difference in the height of the column corresponding with an equal difference of

percentages in solution will be nearly the same with salts of the same molecular weight, but larger with increasing molecular weight of the salt in solution. For example, with change of percentage of sodium chloride from 23·4 to 5·8 there is a difference of 2·6 mm. in the height of the column of liquid, whereas for the same change in a solution of potassium chloride the difference in the height of the column is 6·9 mm. The author proposes to investigate in the same way solutions of carbon compounds, and especially solutions of salts containing water of crystallisation.
B. B.

Catalytic Action of Metals on Oxyhydrogen Gas and the Occlusion of Hydrogen. By A. Berliner (*Ann. Phys. Chem.* [2], **35**, 791—810).—The term catalysis was first applied by Berzelius (*Ann. Chim. Phys.*, **37**, 66) to the power shown by certain substances of causing decomposition or other chemical changes in other substances without being themselves affected.

Dulong and Thénard have shown (*Ann. Phys Chem.*, **76**, 81) that all metals and some earths can determine chemical union between oxygen and hydrogen at temperatures below the boiling point of mercury, and in the case of platinum, palladium, rhodium, and iridium, at ordinary temperatures. Faraday has shown (*Ann. Phys. Chem.*, **33**, 149) that the action of platinum on oxyhydrogen gas occurs at ordinary temperatures, only when the surface of the metal is perfectly clean.

Henry (*Phil. Mag.* [3], **6**, 354) and Turner (*Annalen*, **2**, 210) have shown that copper and iron turnings, zinc-foil and wood-carbon have the same effect on oxyhydrogen gas, but only at temperatures not far below the boiling point of mercury, and Loew (*J. pr. Chem.* [2], **11**, 372) has shown that glass begins to act in the same way at about the same temperature.

Berthelot (Abstr., 1882, 1022) pointed out the connection existing between catalytic action and occlusion of hydrogen, and the present paper contains an account of an extensive series of experiments directed to the further elucidation of the subject. The author arrives at the conclusion that these catalytic actions are invariably due to the occlusion of hydrogen, which when occluded always seems to act in the same way as when in the nascent state, as Graham (*Phil. Mag.* [4], **32**, 503) showed conclusively in the case of palladium. The fact that when the metallic surface is not clean catalysis still takes place at high temperatures is attributed by the author to the partial removal of the film of impurity when the temperature is sufficiently increased; this is in accordance with Graham's observation that the largest amount of gas was occluded when the metal was first strongly heated and then allowed to cool in the gas forming the subject of experiment.
G. W. T.

Metallic Lustre. By W. Spring (*Bull. Soc. Chim.*, **50**, 218—221).—When finely powdered bismuth sulphide, copper sulphide, or manganese peroxide are compressed in cylinders, they acquire a metallic lustre, whilst zinc sulphide, mercury oxide, and copper carbonate acquire a vitreous lustre. A microscopic examination showed that the substances which take a metallic lustre form, without exception, opaque powders, and that the compounds which have glazed surfaces are more or less transparent when finely powdered. Between metallic and vitreous lustre there are all degrees corresponding with the various degrees of transparency and opaqueness. The metallic lustre, therefore, does not depend on the chemical but on the physical state of a substance (compare Dove, *Ann. Phys. Chem.*, **83**, 169; Brewster, *Fortschritte d. Phys.*, **8**, 331; and Brücke, *ibid.*, **17**, 313).

N. H. M.

Apparatus for Fractional Distillation in a Vacuum. By J. W. BRÜHL (*Ber.*, **21**, 3339—3342).—The apparatus consists of a cylindrical vessel, closed at the bottom and provided at the top with a ground flange, on to which fits a lid provided with a corresponding flange and two tubulures, one of which is placed in the centre of the lid. Through the centre tubulure, closed by an india-rubber cork, passes a rod by means of which a circular rack containing test-tubes can be rotated in order to bring the tubes in turn immediately under the condenser-tube which passes through the second tubulure, also closed by an india-rubber cork. The cylindrical vessel is provided with a tubulure for connection to a pump.

W. P. W.

Ether Levels. By R. WEBER (*Ber.*, **21**, 3448—3451).—The crystalline figures frequently observed in the ether levels attached to levelling instruments or physical apparatus, are caused by the use of wet ether, and of glass which is readily attacked by water. Three kinds of glass having the composition—

	SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	Total.
Relatively hard ...	69·00	0·89	12·21	18·52	—	100·62
Relatively soft	65·42	0·93	13·67	19·76	—	99·78
Bonsack glass	69·93	0·94	4·56	7·27	17·30	100·00

were experimented with, and it was found that tubes of Bonsack glass were attacked both by wet and dry ether, and gave crystalline figures within a month of being filled; that tubes of the softer potash glass were also readily attacked by wet ether, but showed only slight indications of crystals after two years when filled with dry ether, whilst tubes of the harder potash glass were also attacked, although more slowly, by wet ether, but remained clear after the lapse of two years when filled with dry ether.

W. P. W.

Inorganic Chemistry.

Oxidation of Hydrogen Iodide by Oxy-acids. By O. BURCHARD (*Zeit. physikal. Chem.*, **2**, 796—839).—This paper contains the details of a large number of experiments on the action of chloric, bromic, and iodic acids on hydrogen iodide, with varying concentrations of the solutions, and also in the presence of other acids. Of the above three acids, iodic acid is the one which acts most readily on hydrogen iodide and chloric acid the least. With dilute solutions of iodic acid and hydrogen iodide, a certain period elapses before the reaction sets in, this period increasing, of course, with the dilution and also with the temperature.

It was necessary in studying the reaction, as a time reaction, to neutralise the mixture of both acids at a given moment, without affecting in any way the liberated iodine. This it was found could be done by the addition of acid sodium carbonate to the solution. The carbonate, which is thus introduced in excess, interferes, however, with the estimation of the iodine by means of thiosulphate, but for the latter, sodium hydrogen sulphite may be substituted, the action of which on iodine in solution is represented by $NaHSO_3 + H_2O + I_2 = NaHSO_4 + 2HI$, and is not affected by the presence of the carbonate.

The action of iodic acid on hydrogen iodide is represented by $5HI + HIO_3 = 3H_2O + 3I_2$. For the action of bromic acid, solutions of at least $\frac{1}{1000}$ normal concentration are required, and the action takes place in three stages: (1) $HBrO_3 + 5HI = 3H_2O + Br + 5I$; (2) $Br + HI = HBr + I$; (3) $HBrO_3 + 5HBr = 3H_2O + 3Br_2$. Hence, if there are less than six equivalents of hydrogen iodide to each equivalent of bromic acid present, bromine will be found in the solution at the end of the reaction. For the action of chloric acid, the solutions must be so concentrated, and the time required is so long, that a decomposition of the hydrogen iodide itself occurs, and thus the exact nature of the reaction cannot be ascertained.

None of the ordinary equations satisfy the conditions of the above changes studied as time reactions. The author finds, however, that the time required for the oxidation of a given quantity of hydrogen iodide depends in a similar manner on the concentration, as the action of sulphurous on iodic acid studied by Landolt (Abstr., 1886, 658). An excess of either acid above the equivalent quantities produces an acceleration of the reaction. The presence of other acids, both those which take part in the reaction and those which do not, also causes an acceleration, which in the case of the latter is in proportion to their avidities.

H. C.

Action of Incandescent Platinum on Gases and Vapours.

By W. R. HODGKINSON and F. K. S. LOWNDES (*Chem. News*, **58**, 223—224; compare Abstr., 1889, 20).—It is now shown that iodine monochloride or trichloride, or chlorine in the presence of iodine or iodine bromides, when vaporised and submitted to the action of incandescent platinum wire, in the manner already described, give rise to flames, to mixtures of platinous chloride or bromide and iodide, and in the presence of chlorine to the deposition of crystals of platinum on the hottest part of the wire. In similar experiments with carbon tetrachloride, there is no flame, chlorine is liberated and carbon and carbon sesquichloride are deposited; with phosphorus pentachloride there is flame, but the wire soon becomes alloyed with liberated phosphorus, and, consequently, melts; with hydrochloric acid, platinous chloride is formed; hydrogen fluoride yields a soluble platinum salt; mercurous chloride gives platinous chloride and mercury; phosphorus or arsenic vapour destroys the wire at once, whilst there is no apparent action with mercury, sulphur, nitrogen oxides, or sulphurous anhydride.

D. A. L.

Analysis of Atmospheric Air. By UFFELMANN (*Chem. Centr.*, 1888, 1324—1325, from *Archiv. f. Hygiene*, 8, 262—350).—The carbonic anhydride was determined in a flask of about 2½ to 4 litres capacity. After filling with water, the flask was completely filled with the air under investigation, by running out the water again and allowing it to drain for 10 minutes. 50 c.c. of baryta-water (7 : 1000) was next added, the flask closed with a tight stopper with india-rubber cap, and after shaking for one minute, allowed to remain by itself for 24 hours. The stopper was now replaced by a double-bored one, 60 c.c. of freshly boiled water added to wash down the sides of the flask, and the excess of baryta titrated with oxalic acid from a burette with a very long nozzle, reaching through the stopper down to the liquid at the bottom of the flask. (The oxalic acid = 2·8636 grams per litre.)

The determination of the organic matters of the atmosphere was made by passing a definite quantity of the air through a solution of potassium permanganate, of which 1 c.c. = 0·395 gram $KMnO_4$ (= 0·1 mgrm. = 0·07 c.c. O = 0·7875 mgrm. oxalic acid) and the excess of permanganate determined by oxalic acid. The dust was collected on an asbestos filter and titrated with permanganate according to the method above mentioned. The micro-organisms were determined, after collecting in sterilised water, according to Esmarch's method.

The ammonia was determined by projecting a spray of water against a slanting glass plate at the distance of 1 metre, and titrating with Nessler's reagent.

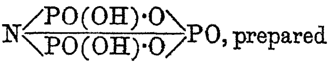
The principal results of a long series of examinations of the atmosphere in the neighbourhood of Rostock are as follows :—(1.) The carbonic anhydride amounted to 3·18 in 10,000 in the open field; the amount increased with land-winds or fog. (2.) The organic matters were equivalent to 2·71 c.c. oxygen per 1,000,000 vols. of air in the open field; this amount varied very greatly, it being decidedly less after continued rain. (3.) The amount of organic matter in the air at the sea-coast was found to be but one-third of that found 12 kilometres inland. (4.) The air of the Rostock University yard contained one-tenth more carbonic anhydride and one-third more organic matter than the air of the open fields. (5.) The air in the open fields near Rostock contained, on the average, 250 micro-organisms per cubic metre, that of the university yard 450, whilst the air on the sea-coast contained but 100 per cubic metre; these quantities being less after continued rain and greater during fog. (6.) The amount of carbonic anhydride in cellars depends greatly on the barometric pressure, and varies inversely as the height of the barometer. (7.) The air of cellars contained spores of fungi. (8.) The air of house sewers was found to be but little richer in organic matter than that of well ventilated rooms, and contained but few germs. (9.) Atmospheric air may be considered impure when it contains so much oxidisable organic matters that in 1,000,000 vols. 12 or more vols. of oxygen are required in the permanganate test. J. W. L.

Hydrogen Telluride. By BERTHELOT and FABRE (*Ann. Chim. Phys.* [6], **14**, 103—106).—Pure hydrogen telluride (compare Bineau, *Ann. Chim. Phys.* [2], **47**, 232) can be prepared by treating magnesium telluride with very dilute hydrochloric acid in an atmosphere of nitrogen. The gas thus obtained is completely and rapidly absorbed by alkalis, yielding white or colourless, crystalline tellurides which dissolve in pure water, forming colourless solutions; if, however, a trace of oxygen is present, violet or purple solutions are produced, and, with a large excess of oxygen, metallic tellurium is immediately precipitated. It is very unstable; when kept over dry mercury, it decomposes in a few hours, even in the dark, but in presence of moist air decomposition is instantaneous. The smell of hydrogen telluride differs considerably from that of hydrogen sulphide or selenide, and when the gas is inhaled the effects produced are far less disagreeable than in the case of the latter. The magnesium telluride referred to above is prepared by the action of excess of tellurium vapour on heated magnesium in an atmosphere of pure, dry hydrogen. It is a white substance, which quickly darkens on exposure to the air, and dissolves in water, forming a blackish-purple solution, owing to the presence of oxygen; it dissolves in water saturated with nitrogen, yielding an almost colourless solution. F. S. K.

Amides of Phosphorus and Sulphur. By A. MENTE (*Annalen*, **248**, 232—269).—Gladstone (this Journal, 1864, 225; 1866, 1 and 290; 1868, 64 and 261, and 1869, 55) obtained a series of compounds by the action of gaseous ammonia on phosphorus oxychloride, which he regarded as amic acids of pyrophosphoric or tetraphosphoric acid. The author considers that these compounds are *imido*-acids. *Imidodiphosphoric acid*, $NH<\substack{PO(OH)\\PO(OH)}>O$ (Gladstone's pyrophosphamic acid), can be prepared by the action of ammonium carbamate on phosphorus oxychloride. The product is dissolved in water containing hydrochloric acid, and the acid is precipitated in the form of the barium or iron salt by the addition of barium or ferric chloride. The *barium* salt contains 1 mol. H_2O.

Di-imidodiphosphoric acid, $NH<\substack{PO(OH)\\PO(OH)}>NH$, is best prepared by adding phosphorus oxychloride diluted with 10 times its volume of benzene to excess of ammonium carbamate. The barium salt is sparingly soluble in water and is anhydrous. A basic sodium salt, $NaN{:}P_2O_2(ONa)_2{:}NH$, is known.

Di-imidodiphosphormonamic acid (pyrophosphotriamic acid), $NH<\substack{PO(NH_2)\\PO(OH)}>NH$, is an insoluble, white powder, obtained by saturating phosphorus oxychloride with ammonia at 100°, and washing the product with water. The acid is decomposed by boiling with sodium hydroxide, yielding the basic sodium salt of di-imidodiphosphoric acid. Silver nitrate gives. with neutral solutions of the acid, the monobasic silver salt, $P_2O_2(NH)_2(NH_2)\cdot OAg$, with ammoniacal solutions a salt of the formula $NAg{:}P_2O_2(NAg)_2(NH_2)\cdot OAg$. The salts of this acid have already been described by Gladstone (*loc. cit.*).



Nitroltrimetaphosphoric acid, $N\begin{matrix}\diagup PO(OH)\cdot O \diagdown \\ \diagdown PO(OH)\cdot O \diagup\end{matrix}PO$, prepared by heating imidodiphosphoric chloride, $NH(POCl_2)_2$, at 290°, yields an insoluble *barium* salt, $NP_3O_7Ba + H_2O$. The *calcium* and ferric salts are insoluble, even in strong acid. Most of the metallic salts are insoluble in water but dissolve in acids. Neither the acid itself nor the salts of the alkali metals have been obtained in a crystalline form.

Ammonium imidosulphonate, $NH(SO_2\cdot ONH_4)_2$, is formed by the action of ammonium carbamate on sulphuryl chloride, pyrosulphuryl chloride, or sulphuric monochlorhydrin. Ammonium chloride is removed by digesting with alcohol, and the residue is recrystallised from water. The compound crystallises in the monoclinic system, and its sp. gr. is 1·965. *Imidosulphurylamide*, $NH(SO_2NH_2)_2$, is the first product of the action of ammonium carbamate on pyrosulphuryl chloride. It is decomposed by water, yielding ammonium imidosulphonate. The amide forms beautiful crystals, and is freely soluble in water. W. C. W.

Allotropic Arsenic. Reply to Geuther. By Engel (*Bull. Soc. Chim.*, **50**, 194—197).—Several new determinations of the specific gravity of allotropic arsenic gave the mean 4·6, which is the same number as that previously obtained (compare Geuther, Abstr., 1887, 888). The ratio of the densities of crystalline and allotropic arsenic is 1·245, and is practically the same as the ratio of white and red phosphorus = 1·244. The molecular constitution of the two modifications of arsenic seems to be the same as that of the corresponding modifications of phosphorus. N. H. M.

Action of Ammonia and Amines on Arsenious Bromide. By W. Landau (*Chem. Centr.*, 1888, 1354—1355).—By passing dry ammonia into a solution of arsenious bromide and benzene, the compound $2AsBr_3,7NH_3$ was formed. *Ethylamine* forms the compound $AsBr_3,4NH_2Et + H_2O$, melting at 152°. *Dipropylamine* forms with it the compound $AsBr_3,4NHPr_2 + H_2O$, melting at 258°. The *trimethylamine*-derivative, $AsBr_3,3NMe_3$, melts at 235°. The compound from *triethylamine*, $AsBr_3,3NEt_3$, melts at 242°. The *aniline* compound, $AsBr_3,3NH_2Ph + H_2O$, becomes changed into $AsBr_3,4NH_2Ph + H_2O$, by treatment with absolute alcohol or glacial acetic acid. *Diphenylamine arsenious bromide*, $AsBr_3,3NHPh_2 + H_2O$, melts at 140°, and becomes changed, like the aniline compound, by the action of alcohol or acetic acid into a compound melting at 230°. The *quinoline* compound, $AsBr_3,C_9NH_7,HBr$, melts at 137°. The *triethylphosphine*-derivative, $AsBr_3,PEt_3,HBr$, melts at 65°. J. W. L.

Preparation of Boron and Silicon. By S. G. Rawson (*Chem. News*, 58, 283).—A mixture of 3·5 grams of boric anhydride and

11 grams of calcium fluoride, is gently heated with concentrated sulphuric acid; the boron fluoride evolved is passed over heated potassium contained in a series of bulbs. Potassium fluoride and boron are formed, and are easily separated by washing with water. Amorphous silicon may be prepared in a similar manner. D. A. L.

Preparation of Silicon. By H. N. WARREN (*Chem. News*, **58**, 215—216).—The author prepares amorphous silicon by passing silicon fluoride over metallic magnesium heated in a combustion tube. Among the other products of the reaction is a magnesium silicide, and by the action of concentrated acids on this, a gas is evolved, which takes fire spontaneously in the air with explosive violence; with feeble acids the gas is not spontaneously inflammable. Owing to the difficulty of eliminating free hydrogen from this gas, its exact composition could not be ascertained; it, however, appears to be a mixture of solid, liquid, and gaseous silicon hydride. D. A. L.

Effect of High Temperature and Pressure on Carbon. By C. A. PARSONS (*Proc. Roy. Soc.*, **44**, 320—323).—Carbon rods were surrounded by benzene, paraffin, treacle, chloride or bisulphide of carbon, and submitted to great pressure in a hydraulic press, the rods being meantime heated by passing an electric current through them. In some cases a considerable amount of gas was evolved, and a soft friable deposit of carbon produced. In no case was the density of the carbon increased. When the rod was surrounded with silica, the latter fused, and the rod was largely converted into graphite; the same occurred with hydrated alumina in lime or magnesia, the rod being rapidly destroyed with evolution of gas. With layers of coke, lime, and silica, the rod was rapidly corroded, and was found after the experiment to be coated with a coke-like layer of great hardness, sufficient to scratch rock-crystal and ruby, and to wear down the cut facets of a diamond. It resists the action of a mixture of hydrofluoric and nitric acids. The conditions of temperature and pressure with presence of moisture, lime, and silica, resemble those which appear to have existed in the craters of the Cape diamond mines. The part played by the lime and silica is not clear. H. K. T.

Formation of Carbon Oxysulphide by the Action of Carbon Bisulphide on Clay. By A. GAUTIER (*Compt. rend.*, **107**, 911—913).—Kaolin previously heated to incipient redness is packed into a large porcelain tube, which is then heated to bright redness, whilst carbon bisulphide vapour is passed through it. The gas which issues from the tube contains 60—64 per cent. of carbon oxysulphide, 35—39 per cent. of carbonic oxide, about 1 per cent. of carbonic anhydride, and traces of hydrogen sulphide, mixed of course with excess of carbon bisulphide vapour. The proportion of carbonic oxide is lower, and the proportion of oxysulphide higher the higher the temperature. The products are passed into a flask half filled with ice-cold water, which condenses the greater part of the bisulphide; then through potassium hydroxide, which absorbs hydrogen sulphide and carbonic anhydride; then through acidified cuprous chloride, which absorbs carbonic oxide, and finally through a 12 per cent. solution of aniline in alcohol, and over pumice and sulphuric acid. Alcoholic aniline has no action on carbon oxysulphide, but readily absorbs carbon bisulphide.

The properties of pure carbon oxysulphide agree mainly with the ordinary description. It has a very faint, somewhat ethereal alliaceous odour. Carbon oxysulphide, as Berthelot observed, combines slowly with ammonia, forming yellow crystals of ammonium oxythiocarbamate, which is decomposed by water. Sodium hydroxide slowly absorbs the gas, and a 35 per cent. solution in contact with excess of the gas yields pale-yellow tabular and acicular crystals of a thiocarbonate, which is decomposed by water, as indicated by the equation $2NaHCSO_2 + H_2O = NaHCO_3 + NaHS + CO_2 + H_2S$.

When carbon oxysulphide is prepared by the action of carbon bisulphide on an oxide, alumina gives the best results, but it becomes too finely divided, and is difficult to manage. It must be heated to a white heat, since even at a cherry-red heat the yield is small. If, however, sulphur vapour is passed over a mixture of alumina and carbon heated to bright redness, almost pure carbon oxysulphide is obtained. Frémy observed that when carbon bisulphide is passed over heated oxides of lead, zinc, iron, and copper, crystalline sulphides are formed. The author finds that only in the case of zinc oxide is any notable quantity of carbon oxysulphide obtained.

After carbon bisulphide has been passed over kaolin, the tube contains brilliant, acicular crystals of silicon sulphide, and somewhat large, hard, lozenge-shaped crystals, which evolve hydrogen sulphide when moistened, and are slowly decomposed by water into alumina and gelatinous silica. They consist of a kind of thiosilicate, some of the oxygen in the kaolin having been replaced by sulphur, whilst some of the silicon has been removed in the form of sulphide.

C. H. B.

Alkaline Aluminates. By K. J. Bayer (*Chem. Zeit.*, **12**, 1209—1210).—When the product of the ignition of alumina and soda in the molecular proportions 1 : 1 is treated with water, pure hydrated alumina, $Al_2O_3,3H_2O$, is spontaneously and continuously deposited until the solution contains alumina and sodium hydroxide in the proportions of 1 mol. of the former to 6 mols. of the latter; the decomposition then proceeds no further, and the solution remains clear. If instead of water a solution of sodium hydroxide, containing as much sodium as is already present in the ignited mixture is employed, then the solution remains quite clear, whether warm or cold, or at rest or in motion, provided it is protected from carbonic anhydride; but in the presence of this gas, or of spontaneously deposited hydrated alumina, this solution behaves in the manner already described. Neither pulverised glass, nor sand, nor granite powder, nor even ordinary gelatinous alumina can initiate this decomposition. If the solutions contain sodium salts with alkaline reaction, the sodium determined by titration is somewhat higher, but the precipitated alumina is always pure. Potassium aluminate behaves in a similar manner. In explanation of these results, the author suggests that the $Al_2O_3,2Na_2O$ and $Al_2O_3,6Na_2O$ are really chemical compounds.

and therefore with the compounds Al_2O_3,Na_2O and $Al_2O_3,3Na_2O$ would indicate the existence of four different alkaline aluminates.

D. A. L.

Porcelain Glazes. By C. Lauth and G. Dutailly (*Bull. Soc. Chim.*, **50**, 221—251).—The first part of the paper contains the results of experiments made with colourless glazes, which are divided into three classes:—(1.) Silicates of a single base associated with silica and alumina. (2.) Silicates of two bases, associated with silica and alumina. (3.) Silicates of several bases together, associated with silica and alumina. In the second part of the paper, experiments with various coloured glazes are described. N. H. M.

Cause of Rails Rusting less Quickly when in Use than when not. By W. Spring (*Bull. Soc. Chim.*, **50**, 215—218).—The preservation of rails, when in use, from rust is not the result of vibratory movement, or of an electric action due to the passage of trains, but is due to the superficial formation of the magnetic oxide produced by the compression of the rust on the metal.

N. H. M.

A Crystalline Subsulphide of Iron and Nickel. By J. B. Mackintosh (*Chem. News*, **58**, 200).—A compound approximating in composition to the formula Fe_4Ni_2S, has been found in fern-like aggregations of small cubical crystals in the cavities in the concretions in the hearth of a shaft furnace used for smelting roasted nickeliferous pyrrhotite. The author's analytical numbers are: Cu 2·20; Ni,Co 26·16; Fe 61·685; S 8·305; SiO_2 0·56; total, 98·91; deficiency and silica being due to adherent slag. D. A. L.

New Fluorine Compounds of Vanadium. By A. Piccini and G. Giorgis (*Gazzetta*, **18**, 186—194).—On dissolving ammonium metavanadate in aqueous hydrofluoric acid and treating the hot liquid with sulphurous anhydride, a blue liquid is obtained, which on neutralising with ammonia and adding ammonium fluoride, yields a bluish, crystalline precipitate. This is collected, washed with a little water, and recrystallised from water; at first monoclinic prisms having the composition of Baker's salt (Trans., 1879, 760) separate, and then small, blue, lustrous crystals; these are monometric octahedra, which dissolve easily in water, yielding a blue solution, from which the salt separates again on the addition of ammonium fluoride. On analysis, it gave results corresponding with the formula $VOF_2,3NH_4F$. The author calls it *octahedral ammonium hydrofluoroxyvanadate*. When dissolved in concentrated hydrofluoric acid and allowed to remain for some days, it deposits crystals of Baker's salt, $VOF_2,2NH_4F + H_2O$. The new salt is also formed at the negative pole, when a solution of ammonium metavanadate, acidified with hydrofluoric acid and mixed with ammonium fluoride, is submitted to electrolysis; or when the mixture is reduced by alcohol. In the latter case, however, the mother-liquors, if exposed to the air after the hydrofluoroxyvanadate has been deposited, yield yellow, octahedral crystals of the composition $VO_2F,3NH_4F$. These can be obtained more easily by dissolving vanadic acid in excess of hydrofluoric acid, and carefully neutralising with ammonia while the liquid is still warm. On cooling, an abundant deposit of the crystals is obtained; care must be taken not to add any great excess of ammonia, otherwise colourless crystals of ammonium vanadate alone will separate.

By adding potassium hydrogen fluoride to a solution of ammonium metavanadate reduced by sulphurous anhydride, and evaporating the blue solution, the author obtained sky-blue, crystalline crusts, of the composition $VOF_2,2KCl$.

The remainder of the paper is devoted to theoretical consideration of the crystallographic connection of various isomorphous fluorides, the author drawing especial attention to the fact that the four compounds $VO_2F,3NH_4F$, $VOF_2,3NH_4F$, $FeF_3,3NH_4F$, and $CrF_3,3NH_4F$, all crystallise in the monometric system in cubes or octahedra, and all contain the same number of atoms. C. E. G.

Mineralogical Chemistry.

A Remarkable Bed of Sulphur. By PREUSSNER (*Chem. Centr.*, 1888, 1339—1340, from *Zeit. deut. geol. Gess.*, **40**, 184—187).—In 1869, when oil was being bored for, an unusually large bed of sulphur was found in Louisiana, one mile from the South Pacific Coast, eight miles from Calcasieu River. Since 1886 four borings have been made, all close together, and with very similar results. The following structure was met with during the first of these:—

	Thickness of bed. feet.	Depth. feet.
Yellow and blue clay	160	160
Grey and yellow sand	173	233
Rock	2	235
Blue sandy limestone	48	383
White soft limestone	60	443
Pure sulphur	108	551
Sulphur accompanying gypsum	99	650
Pure sulphur	6	656
Sulphur accompanying gypsum	24	680
Gypsum rich in sulphur	440	1130
Sulphur accompanying gypsum	100	1230

J. W. L.

Arsenopyrite from Servia. By J. LOCZKA (*Zeit. Kryst. Min.*, **15**, 40—41).—The crystals analysed by the author had the following percentage composition:—

S.	Sb.	As.	Fe.	Zn.	Insoluble.	Total.
21·71	0·14	42·38	34·58	0·46	0·22	99·49

The insoluble residue consists of silica with a trace of calcium. The sp. gr. of the mineral is 6·0594. B. H. B.

Constitution of Arsenopyrite. By J. LOCZKA (*Zeit. Kryst. Min.*, **15**, 41—42).—When heated without access of air, arsenopyrite loses much of its arsenic, the loss amounting to 40·55 per cent. The author has made a series of experiments to ascertain the chemical changes that take place when arsenopyrite is heated, and concludes that in this mineral an iron sulphide must be present, which loses when heated a portion of its sulphur. The latter then renders the arsenic free by combining as iron sulphide with the iron that was present in combination with arsenic. As analysis shows the composition of arsenopyrite to correspond with the ratio 1Fe : 2S,1Fe : 2As, it must be supposed that this iron sulphide is FeS_2, and consequently that arsenopyrite consists of $FeAs_2$ and FeS_2. The decomposition brought about by the action of heat may be illustrated by the following equations:—(1.) $FeAs_2 + FeS_2 = FeS + S + FeAs_2$. (2.) $FeAs_2 + S = FeS + 2As$. (3.) $FeAs_2 + FeS_2 = 2FeS + 2As$.

B. H. B.

Periclase from Nordmarken. By A. SJÖGREN (*Zeit. Kryst. Min.*, **15**, 106, from *Geol. Fören. Förh.*, **9**, 527).—Periclase occurs with hausmannite in large and small grains in a bed of limestone in a manganese mine in Nordmarken. The mineral is colourless and transparent, but is usually coloured green by admixed minerals. Analysis gave the following results:—

MgO.	MnO.	ZnO.	FeO.	Total.
87·38	9·00	2·52	0·19	99·09

B. H. B.

Psilomelane. By G. LANGHAUS (*Jahrb. f. Min.*, i, Ref., 16—17).—The author has analysed three varieties of psilomelane with the following results:—

	BaO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Al_2O_3.	Fe_2O_3.
I.	0·61	1·18	0·52	2·59	0·18	3·06	1·16	0·37
II.	6·50	0·52	0·66	2·17	0·76	3·90	0·87	0·49
III.	6·43	1·33	0·21	1·89	0·69	3·10	1·10	0·50

MnO.	O.	SiO_2.	Insoluble.
74·37	15·06	0·38	0·21
69·76	13·93	2·72	0·24
67·29	12·19	3·12	2·47

Traces of CoO, NiO, CuO, PbO were also observed in each case, and of Li_2O in II and III. The varieties analysed were obtained (I) from the Volle Rose mine, Mittelberg, in the Duchy of Gotha, (II) from the Heinrichsglück mine, Rumpelsberg, Gotha, and (III) from Eisenbach, near Neustadt, in the Black Forest. Qualitative analyses of psilomelane from other mines in the Duchy of Gotha led to similar results. The author calculates the formula of psilomelane to be H_2MnO_3.

B. H. B.

Analyses of Monazite and Xenotime. By C. W. Blomstrand (*Zeit. Kryst. Min.*, 15, 99—103, from *Geol. Fören. Förh.*, 9, 160).—The author gives the results of the analyses of nine specimens of monazite from Norway. The localities from which the specimens were derived were Moss, Dillingsö, Lönneby, Arendal, Narestö, and Hvalö. The analyses show that monazites are normal salts of tribasic phosphoric acid. There is, however, an excess of bases, which appear to be in combination with silica. The general formula of these minerals is therefore $m(3RO,P_2O_5) + 2RO,SiO_2 + pH_2O$, in which m is between 5 and 20, and p usually less than 1. The author's conclusion is that monazites are normal cerium and thorium phosphates, in which a portion of the phosphoric acid is replaced by silica. This view is not in accord with that of Penfield, who regards monazites as cerium phosphates with mechanically admixed thorite. In an appendix, the author gives two analyses of xenotime from Hvalö and Narestö, and concludes that the composition of this mineral is similar to that of monazite. B. H. B.

Sulphohalite, a New Sodium Sulphato-chloride. By W. E. Hidden and J. B. Mackintosh (*Amer. J. Sci.*, 36, 463—464).—This mineral belongs to the regular system, and occurs in rhombic dodecahedra. It is transparent, with a faint yellow colour. Its sp. gr. is 2·489, and its hardness 3·5. Analysis yielded the following results:—

Cl.	SO_3.	Na_2CO_3.
13·12	42·48	1·77

The formula is $3Na_2SO_4,2NaCl$. Excepting the very rare Cornish mineral connellite, no other species is known of analogous composition. The mineral was found with hanksite at Borax Lake, San Bernardino Co., California. Only three examples are known, and two of these are in the collection of C. S. Bement, of Philadelphia. The authors propose for this new mineral the name of sulphohalite as indicating its remarkable composition.

B. H. B.

Allactite from Långban. By A. Sjögren (*Zeit. Kryst. Min.*, 15, 106—107, from *Öfvers. Vet. Akad. Förh.*, 1887, 107).—This mineral occurs, with a manganiferous barytes, calcite, and a mineral resembling aphrodite, at the Collegii mine at Långban. It resembles the allactite found at Nordmarken. On analysis, it gave the following results:—

As_2O_5.	MnO.	CaO.	MgO.	H_2O.	Total.
29·00	58·87	1·77	1·35	9·00	99·99

B. H. B.

Pyrrhoarsenite and Berzeliite. By A. G. Högbom (*Zeit. Kryst. Min.*, 15, 105—106, from *Geol. Fören. Förh.*, 9, 397).—Two specimens of pyrrhoarsenite were analysed; one being the usual orange variety (1), and the other a purer yellow, transparent variety (II) having a sp. gr. of 4·01. Both contained admixed barytes and calcite. The berzeliite (III) examined was a honey-yellow isotropic variety from Långban.

	CO_2.	$BaSO_4$.	FeO.	MnO.	CaO.	MgO.	As_2O_5.	Sb_2O_5.	Total.
I.	1·27	3·96	trace	19·18	18·35	3·50	50·92	2·60	99·78
II.	1·58	1·36	—	14·12	18·54	7·53	53·39	2·90	99·42
III.	—	0·49	—	5·68	19·97	16·12	57·59	—	99·85

B. H. B.

Pyrrhoarsenite and other Swedish Antimoniates. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, i, Mem., 48—53).—The bright straw-yellow anhydrous arsenate from the Sjö mine, in the parish of Grthyttan, Örebro, Sweden, is undoubtedly pyrrhoarsenite, but with double the amount of antimonic acid contained in the yellow variety (Analysis II) discovered by Högbom in 1885. The analysis gave the following results (I) :—

	As_2O_5.	Sb_2O_5.	CaO.	MnO.	MgO.	Total.
I.	53·23	6·54	20·21	10·82	9·20	100·00
II.	56·40	3·07	17·50	15·03	8·00	100·00

The author considers the formulæ of the antimoniates and antimonio-arsenates hitherto found in Sweden to be as follows :—

Pyrrhoarsenite (type I, analysed by Högbom), $20(Ca,Mg,Mn)_3As_2O_8 + Ca_2Sb_2O_7$.

Pyrrhoarsenite (type II, analysed by the author), $10(Ca,Mg,Mn)_3As_2O_8 + Ca_2Sb_2O_7$.

Polyarsenite (Abstr., 1887, 347), $40H_2Mn_4As_2O_{10} + (Ca,Mg)_2Sb_2O_7$.

Xanthoarsenite (Abstr., 1886, 25), $16(Mn,Mg,Fe,Ca,H_2)_{10}As_2O_{15} + (Ca,Mg)_2Sb_2O_7$.

Manganostibiite, $2(Mn,Fe,Ca,Mg)_3As_2O_8 + 5(Mn,Fe,Mg)_{10}Sb_2O_{15}$.

Hæmatostibiite, $Mg_2Sb_2O_7 + 5(Mn,Fe)_{10}Sb_2O_{15}$.

Atopite, $(Ca,Na_2,Fe,Mn,K_2)_2Sb_2O_7$.

Monimolite, type I (Nordenskiöld), $Pb_3Sb_2O_8$; type I (Igelström), $(Pb,Fe,Ca,Mg)_4Sb_2O_9$; type II (Flink) $(Pb,Fe,Mn)_3Sb_2O_8$.

(Compare Abstr., 1888, 565.) B. H. B.

Thioantimonites from Colorado. By L. G. EAKINS (*Amer. J. Sci.*, **36**, 450—453).—The author gives the results of the analyses of two thioantimonites from Gunnison Co., Colorado. The first (Analysis I) was found in the Domingo mine, on the ridge between Dark Cañon and Baxter Basin. It consists of aggregates of small, acicular crystals, forming wool-like masses in the cavities of a highly decomposed siliceous gangue. It is dull, greyish-black in colour, and no crystalline form could be distinguished. Its formula is $3(Pb,Fe)S,2Sb_2S_3$. The second specimen was found at a mine on Augusta Mountain. It occurs in a siliceous gangue with iron pyrites and zinc blende, and forms groups of acicular crystals, which are deeply striated, elongated prisms. Its formula is $5PbS,2Sb_2S_3$. It thus appears to be a freieslebenite in which the silver has been completely replaced by lead. The analytical results were as follows :—

	Ag.	Cu.	Pb.	Fe.	Mn.	Sb.	S.	Insoluble.	Total.
I.	Trace	trace	39·33	1·77	trace	36·34	21·19	0·52	99·15
II.	Trace	—	55·52	trace	—	25·99	18·98	—	100·49

B. H. B.

Hjelmite. By M. Weibull (*Zeit. Kryst. Min.*, **15**, 104—105, from *Geol. Fören. Förh.*, **9**, 371).—This mineral crystallises in the rhombic system, the axial ratio being $a : b : c = 0·465 : 1 : 1·026$. The specimens examined were considerably altered, and were seen under the microscope to consist of an amorphous substance containing black metallic grains of unaltered hjelmite. Analysis gave results corresponding with the formula $4RO,3R_2O_5 + 2H_2O$.

B. H. B.

Eudidymite. By A. E. Nordenskiöld (*Zeit. Kryst. Min.*, **15**, 107—108, from *Geol. Fören. Förh.*, **9**, 434).—Eudidymite was discovered in 1887 in the Island of Upper Arö in the Langesundsfjörd. According to Brögger it is monoclinic, with the axial ratio of $a : b : c = 1·71069 : 1 : 1·107113$; $\beta = 86° 14' 27''$. Analysis gave the following results:—

SiO_2.	BeO.	Na_2O.	H_2O.	Total.
73·11	10·62	12·24	3·79	99·76

B. H. B.

Analysis of Natrolite. By G. Lindström (*Zeit. Kryst. Min.*, **15**, 108, from *Geol. Fören. Förh.*, **9**, 434).—This analysis was made in order to determine whether the so-called brevicite that accompanies the eudidymite of Arö (see preceding Abstract) also contained beryllium. This was, however, not the case. The analytical results were as follows:—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	H_2O.	Total.
47·92	26·80	16·25	0·26	9·51	100·74

B. H. B.

Hyalotekite from Langban. By G. Lindström (*Zeit. Kryst. Min.*, **15**, 96—97, from *Öfvers. Sv. Vet. Förh.*, 1887, 589).—The hyalotekite described by Nordenskiöld has been analysed by the author with the following results:—

SiO_2.	PbO.	BaO.	CaO.	CuO.	MnO.	BeO.	MgO.	K_2O.	Na_2O.
39·47	25·11	20·08	7·82	0·09	0·29	0·75	0·09	0·89	0·17

Al_2O_3.	Fe_2O_3.	B_2O_3.	F.	Cl.	Ignition.	Total.
0·18	0·06	3·73	0·99	0·06	0·59	100·37

The formula deduced from these results is $12(RO,2SiO_2) + 3RO,2B_2O_3 + RF$ B. H. B.

Gadolinite. By C. Rammelsberg (*Jahrb. f. Min.*, 1889, i, Ref., 25—26, from *Sitzb. preuss. Akad. Wiss.*, 1887, 553).—The author has analysed specimens of gadolinite from Hitterö (I) and from Ytterby (II) with the following results:—

	SiO_2.	Y_2O_3.	Ce_2O_3.	Fe_2O_3.	FeO.	BeO.	CaO.	Loss on ignition.	Total.
I.	24·36	45·51	7·01	2·85	11·50	8·58	0·36	0·50	100·67
II.	25·35	38·13	13·55	4·07	7·47	10·03	0·57	1·34	100·51

The gadolinite from Hitterö occurs in large, black crystals; sp. gr. 4·448 to 4·490; that from Ytterby has a vitreous or amorphous nature, and brilliant lustre; sp. gr. 4·212. The formula of both varieties is $R''_5R'''_2Si_4O_{19}$. Gadolinite thus approaches datolite and euclase in composition.

B. H. B.

Mineralogical Notes. By A. E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, **15**, 97—98, from *Geol. Fören. Förh.*, **9**, 26).—1. *Alvite and Anderbergite.*—Alvite from Alve, near Arendal, gave on analysis the following results:—

SiO_2.	Metallic* acids.	PbO.	Fe_2O_3.	MnO.	Ce_2O_3.	Y_2O_3.	BeO with some Al_2O_3.
26·10	2·78	0·45	5·51	0·27	3·27	1·03	14·73

ZrO_2.	CaO.	MgO.	Loss on ignition.	Total.
32·48	2·44	1·05	8·84	98·95

This mineral is absent from the felspar mines of the pegmatite veins. It is, however, replaced by a somewhat similar mineral, which the author regarded as cyrtolite, but which Blomstrand claims to be a new species to which the name of anderbergite should be given. (See following Abstract.)

2. An analysis of monoclinic crystals of hydrargillite from Langesund in Norway, gave the following results:—

Al_2O_3.	SiO_2.	H_2O.	Total.
65·90	0·43	33·57	99·90

3. *Diaspore from Horrsjöberg in Wermland.*—An analysis of this mineral, supposed to be identical with Igelström's new mineral "empholite," gave, when corrected for admixed cyanite and pyrophyllite, 84·32 per cent. of alumina and 15·68 per cent. of water.

B. H. B.

The so-called Cyrtolite of Ytterby. By C. W. BLOMSTRAND (*Zeit. Kryst. Min.*, **15**, 83, from *Sv. Vet. Akad. Handl.*, **12**, 1—10).—Four analyses of massive somewhat impure material gave the following mean results:—

SiO_2.	ZrO_2.	Y_2O_3.	Ce_2O_3.	FeO.	CaO.	MgO.	CuO.	Na_2O.	H_2O.	Total.
26·93	41·17	10·93	trace	1·54	5·85	trace	0·17	0·89	12·55	100·03

The results were obtained after 10·51 per cent. of phosphates, &c., regarded as impurities, had been subtracted. The formula is $R_3Y_2Zr_9(SiO_4)_{12} + 18H_2O$. The analysis agrees so well with that of crystals by Nordenskiöld, that the author cannot regard the mineral merely as an altered zircon, but considers it a distinct mineral species.

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* Metallsaüre.

and, as its composition differs considerably from that of the American cyrtolite, proposes for it the name of *Anderbergite*. B. H. B.

Swedish Minerals. By G. Flink (*Zeit. Kryst. Min.*, **15**, 88—92, from *Sv. Vet. Akad. Handl.*, **13**, 1—94).—1. The author gives the following new analysis of manganese-epidote:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MnO.	H_2O.	Total.
36·44	24·65	12·44	19·52	4·52	3·19	100·76

The crystals of this mineral occur with titanite, barytes, and manganophyll in fissures filled with calcite, in a matrix consisting of berzeliite, calcite, and manganese-epidote. On the crystals, the author has determined the following new forms: $0P$, $\infty\bar{P}\infty$, $\frac{1}{2}\bar{P}\infty$, $\bar{P}\infty$, $-\frac{1}{2}\bar{P}\infty$, ∞P, $\infty\grave{P}2$, P, $\grave{P}\infty$. With regard to its composition and most of its optical properties, manganese-epidote forms a link between ordinary epidote and piemontite.

2. Manganophyll occurs at Långban in small copper-coloured scales intimately mixed with magnetite and iron-glance, as well as in crystals with tephroite and magnetite in fissures filled with calcite. The analysis gave the following results:—

SiO_2.	F.	MgO.	MnO.	Fe_2O_3.	Al_2O_3.	K_2O.	Na_2O.	H_2O.	Total.
41·36	0·49	13·27	5·41	4·66	16·02	11·43	2·09	4·62	99·33

Manganophyll is thus shown to differ considerably from all the micas hitherto described.

3. The author gives the following analyses of (I) hornblende and (II) grammatite from Nordmarken:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Total.
I.	49·81	7·83	8·90	13·89	0·95	4·75	12·89	99·82
II.	55·77	—	—	2·95	—	24·73	15·92	99·37

The hornblende seems to contain of 50 per cent. $Ca(Fe,Mg,Mn)_3Si_4O_{12}$, 37·5 per cent. $Ca(Al,Fe)_2Si_4O_{12}$, and 12·5 per cent. $Ca(Al,Fe)_2SiO_6$. Of these compounds, the first is the ordinary actinolite-silicate, whilst the two others have not hitherto been identified in the hornblende series. The formula of the grammatite is $Ca(Mg,Fe)_3Si_4O_{12}$.

B. H. B.

Auerlite, a new Thorium Mineral. By W. E. Hidden and J. B. Mackintosh (*Amer. J. Sci.*, **36**, 461—463).—This mineral has hitherto been found at only two places in Henderson Co., North Carolina, namely, at the Freeman mine, and on the Price land, three miles to the south-west. At both places it occurs in disintegrated granitic or gneissic rock, intimately associated with zircon crystals, on which it is often seen implanted. The crystals are tetragonal, lemon-yellow to brown-red in colour, and sub-translucent to opaque. The mineral is very brittle; its hardness is 2·5 to 3, and its sp. gr. 4·422 to 4·766, the darker crystals having the greatest density. Analysis gave the following results:—

H_2O.	CO_2.	SiO_2.	P_2O_5.	ThO_2.	Fe_2O_3.	CaO.	MgO.	Al_2O_3.	Total.
10·21	1·00	7·64	7·46	70·13	1·38	0·49	0·29	1·10	99·70

The formula is $ThO_2,SiO_2,\frac{1}{3}P_2O_5,2H_2O$, or that of a thorite in which part of the silica is replaced by phosphoric acid. As this mineral was found while mining the zircons necessary to supply the demand caused by the invention of the system of incandescent gas-lighting of Carl Auer v. Welsbach, the authors propose to name it *Auerlite* in his honour. B. H. B.

Phosphatic Deposits at Montay and Forest. By J. LADRIÈRE (*Compt. rend.*, **107**, 960—961).—At Montay and Forest there is a chalky conglomerate covered by a sandstone containing glauconite. The sandstone is from 0·3 to 1·8 metre thick, and contains 15 to 17 per cent. of phosphoric anhydride. The conglomerate is less rich in phosphates. C. H. B.

Composition of Piperno of the Collina del Vomero. By G. FREDA (*Chem. Centr.*, 1888, 1340, from *Rend. R. Inst. Lombardo* [2], **2**, 177—180).—The grey porous part (I) of the rock has the same composition as the compact part (II). The composition is almost the same as that of the piperno from Pianura, but very different from the tuff of Campi Flegrei. The analytical results of the piperno of Vomero are as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Cl.
I.	62·51	18·44	3·88	0·83	0·47	4·98	7·17	0·22
II.	61·65	19·06	4·14	1·28	0·62	5·31	6·72	—

J. W. L.

Metamorphic and Plutonic Rocks at Omeo. By A. W. HOWITT (*Jahrb. f. Min.*, 1889, i, Ref., 122—125, from *Trans. R. S. Victoria*).—About a mile from the northern end of the Hinnomugie Marsh there is a small tributary of Livingstone Creek in which the contact of muscovite granite and a greyish, fine-grained mica-schist is visible. The latter is seen under the microscope to consist of muscovite, brown mica, and tourmaline, or, in other places, of these minerals and quartz. The granite contained yellow microperthite (Analysis I), and silver-white mica (Analysis II).

Several miles to the south-east of this locality, at Wilson's Creek, a series of rocks consisting of mica-schists and gneisses have been collected. They are traversed by eruptive rocks, and at the contact have been subject to various changes. An analysis (III) is given of a finely granular mica-schist, which under the microscope is seen to consist of colourless mica, yellowish magnesia-mica, a little quartz in grains, and graphite. In the author's opinion, this and similar rocks are metamorphosed Lower Silurian sedimentary rocks. An analysis (IV) is also given of a graphic granite, consisting of microcline, quartz, secondary muscovite, and albite.

	Fe.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.
I.	—	62·13	24·35	trace	—	—	—	6·66	8·31
II.	0·15	44·67	37·44	0·48	0·91	0·26	0·42	1·24	10·90
III.	—	64·00	19·82	3·50	—	0·32	2·14	1·10	4·41
IV.	—	70·91	15·32	trace	—	0·58	0·07	2·31	10·07

	H_2O.	C.	P_2O_5.	Total.	Hygroscopic water.	Sp. gr.
I.	0·50	—	—	101·95	—	—
II.	3·76	—	—	100·23	2·18	2·768
III.	2·23	3·32	0·10	100·94	0·85	2·651
IV.	0·51	—	—	99·77	0·15	2·564

B. H. B.

Composition of some Rocks from the Shore at Nice. By C. Montemartini (*Gazzetta*, **18**, 170—179).—These rocks, which were collected soon after the earthquake of February 23rd, 1887, are 31 in number, and may be divided into seven groups, of which a minute detailed description is given.

1. *Augite-andesite.*—The 10 specimens of this rock, mostly collected at Capo d'Aglio, near Monaco, are of irregular granular structure, in the brown or grey ground-mass of which it is easy to distinguish crystals of augite and of triclinic felspar; magnetite is also present. The sp. gr. of the specimens varied from 2·64 to 2·83. The silica varied for 54·38 to 55·89 per cent.

2. *Andesites which contained both Augite and Hornblende.*—Of the 11 specimens examined, 5 came from Capo d'Aglio, and 6 from the neighbourhood of Antibo. Some of these were homogeneous and compact, of greyish-black colour, and sp. gr. 2·65 to 2·70; magnetite was present. The results of analysis gave—

SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Alkalis.	Loss on ignition.
55·50	7·78	19·57	7·67	2·76	4·30	2·42

The alkali was estimated by difference.

The other samples were altered and not homogeneous, and contained besides augite and felspar, crystals of hornblende, magnetite, and apatite.

3. *Andesites of Trachytic Appearance.*—These were yellowish-white, of granular structure, and contained basaltic hornblende and a large quantity of vitreous, crystalline grains of triclinic felspar. The sp. gr. of one specimen was 2·49, and it contained 2·96 per cent. of water and 53·98 of silica.

4. *Andesite-conglomerate.*—The two specimens of this rock have the appearance of a conglomerate formed from fragments of andesite, the rock is much weathered, but neither by analysis nor by microscopical examination could any cementing material be discovered.

5. *Basaltic-augite.*—This has the same composition as the augite-andesite, but differs from it in not being granular in structure, but compact.

6. *Andesite coated with Gypsum.*—This has a sp. gr. of 2·52, and contains 5·13 per cent. of water and 60·04 of silica.

7. *Compact-semiopal.*—This rock is compact, of light greenish-brown, with resinoid lustre and conchoïdal fracture, and is nearly as hard as quartz. Its sp. gr. is 2·22, and it contains 2·26 per cent. of water and 91·18 of silica. C. E. G.

Examination of the Rocks of the Vulsinian Volcanoes. By L. Ricciardi (*Gazzetta*, **18**, 268—288).—The author has analysed a large number of rocks from the extinct Vulsinian volcanoes, and gives full details of their composition and of the results of their examination both macroscopically and microscopically. From the results obtained now and in former researches, and a comparison of these Vulsinian rocks with those of other volcanic districts, the author considers that most, if not all, of the volcanoes of the Italian peninsula, in very early periods, emitted trachytic and other acid rocks which were succeeded by those of basic character. It would seem, moreover, that the volcanic rocks of the Alpi-Sila group differ in some respects in chemical composition from those of the insular volcanoes of the Pilla group. The different basic lavas of the Alpi-Silla group are almost identical in composition, so that it would seem probable that they have a common origin. The acid rocks of trachytic type of Amiata, Bolsena, and Cimini are almost identical in composition with the trachytes and tufas of Campi Flegrei. C. E. G.

Meteorite from Novo-Ureï. By M. Erofeéff and P. Latschinoff (*J. Russ. Chem. Soc.*, 1888, **20**, 185—213).—This meteorite fell on September 10, 1886, near Novo-Ureï, Penza, together with two other aerolites, the larger of which fell into water, and the smaller was powdered and devoured by the superstitious moujiks. The fragment investigated weighed 1900 grams, and its sp. gr. was found to be 3·463 at 16°. On being powdered for analysis, it was found to contain extremely hard particles which scratched the agate mortar and pestle. It does not yield anything to neutral solvents, such as water, alcohol, and ether, but partly dissolves in hydrochloric acid with liberation of hydrogen and hydrogen sulphide, owing to the presence of iron and probably of magnetic pyrites. Aqua regia dissolves only 70—75 per cent.; and even when the insoluble residue is treated with hydrofluoric and sulphuric acids from 2—2·5 per cent. of a blackish-grey powder remains undissolved. It contains graphite and another substance, which is very hard, and was found to be capable of being burned in oxygen. An elementary analysis made in this way gave its composition: carbon 89·56 per cent., ash 10·44 per cent. Another portion remaining after fusion with potassium pyrosulphate gave: carbon 95·40, ash 3·23. In order to test it for different allotropic modifications of carbon, the residue was treated with strong nitric acid and potassium chlorate, but Brodie's graphitic acid was not formed, although 40 per cent. of the residue dissolved after three treatments. The residue was now whiter, and its sp. gr. was found on an average to be 3·1, which, considering the small quantity used, agrees well with that of diamond (sp. gr. 3·5). The powder was found to be harder than corundum, as the last polished and unpolished faces) is scratched by it very perceptibly.

The meteorite contains therefore diamond (*carbonado*) together with some soft carbon. The total quantity of diamond in the meteorite is no less than 1 per cent. = 85·4 carats. Analysis of the meteorite gave—

Ni.	Fe.	FeO.	MnO.	Al_2O_3.	Cr_2O_3.	MgO.	CaO.	S.	P.
0·20	5·25	13·35	0·43	0·60	0·95	35·80	1·40	0·15	0 02

SiO_2.	C.	Soft.	Hard (carbonado).	Total.
39·51	2·26	=(1·26	1·00)	99·92

Assuming that the sulphur is present as magnetic pyrites and adding phosphorus to nickel-iron, the composition is—

Ni,Fe.	Cr_2O_3.	Fe_7S_8.	C.	Silicates.	Total.
5·47	0·95	0·43	2·26	90·76	99·87

It was shown further, that 67·48 per cent. of the meteorite consist of olivine, of the following percentage composition:—

Mg_2SiO_4.	Fe_2SiO_4.	Ca_2SiO_4.	Mn_2SiO_4.
72·93	24·48	1 89	0·70

Another constituent is augite, to the extent of 23·82 per cent. of the mass of the meteorite. Chromium is present partly in the metallic state, 0·2 per cent. being dissolved in cold hydrochloric acid; partly as chrome-iron ore, 0·65 per cent. A table shows the way in which the different constituents are distributed in the meteorite. The paper contains moreover an account of the microscopic examination of the meteorite, which shows that the mass contains among other ingredients, small, transparent octahedra, in some of which very small black grains were found. They *may* consist of diamond, but unfortunately the carbon residue obtained in the analysis of the meteorite, after treatment with Brodie's solution (see above), consists of almost black particles of an irregular form. With high magnifying power, they appear to be partly transparent and without action on polarised light, but no trace of crystalline form could be detected. In conclusion the authors discuss different cases of occurrence of carbon in meteorites. Pantsch and Haidinger (1846) found cubes of graphite in the Arva iron (Hungary), and regard them as pseudomorphs after iron pyrites, but G. Rose has shown, that this mineral is not found in meteorites, and the forms are besides quite different. Rose thought the graphite cubes may be pseudomorphs after diamond, especially as an analogous allotropic change takes place when diamond is strongly heated in absence of air. G. Rose's prediction is thus confirmed by the results of the present investigation, diamond, however, being found in meteoric stones, whereas it was sought in meteoric irons. Fletcher (see Abstr., 1887, 30) has described graphite in cubic forms as a new mineral, cliftonite, found in the Youndegin meteorite, but this is totally different in properties from the modification of carbon occurring in the Novo-Ureï meteorite. The authors find, after comparison with known classes of aerolites, that the meteorite described above differs from all of them in many points, and propose to name this form *ureïlithe*. B. B.

Black Rivers in Equatorial Regions. By A. MUNTZ and V. MARCANO (*Compt. rend.*, **107**, 908—909).—In the equatorial regions of South America, there are several rivers the water of which is black. Some of the tributaries of the Orinoco and Amazon show this peculiarity. The rocks forming the banks of these rivers remain white, whilst the banks of several ordinary rivers become dark coloured. The black rivers do not impart their colour to the waters with which they mix. They flow through a granitic district covered with a luxuriant, tropical vegetation. The water has a fresh agreeable taste, and remains perfectly limpid even after two months. It contains 0·028 gram per litre of black organic matter similar to that formed in peat bogs, and has an acid reaction which increases when the water is concentrated. It contains no calcium and no nitrates, and the inorganic matter, which consists of silica and oxides of iron, manganese, aluminium, and potassium, with traces of ammonia, does not exceed 0·016 gram per litre. The waters retain their colour for a long time, because in the absence of calcium salts there is no nitrification, and the acid reaction and high degree of aeration prevent putrefaction.

C. H. B.

Organic Chemistry.

Mineral Matter in Natural Petroleums. By J. A. LE BEL (*Bull. Soc. Chim.*, **50**, 359—361).—Bitumen was extracted from a bituminous limestone from Lobsann in Alsace by means of light petroleum; the greater part of the light petroleum was then distilled off, and the rest treated with amyl alcohol which precipitated a black resin. This was again dissolved in light petroleum, precipitated with amyl alcohol, and the solid precipitate washed with ether which removed a reddish resin. The asphaltene so obtained contains 5·4 per cent. of ash. The latter contains 13 per cent. of silica, 17 per cent. of ferric oxide with traces of manganese, and the rest consists chiefly of lime and calcium sulphate.

Asphaltene from the natural oil of Coloméa in Galicia contains only traces of mineral matter.

N. H. M.

Oxidation of the Hydrocarbons, C_nH_{2n-2}. By G. WAGNER (*Ber.*, **21**, 3343—3346; comp. Abstr., 1888, 665).—When diallyl is oxidised with potassium permanganate in dilute aqueous solution, it yields, in addition to a trace of an aldehyde, a mixture of two *hexylerythrols*, $C_6H_{10}(OH)_4$, which can be separated by fractional crystallisation, on adding successive quantities of ether to their solution in absolute alcohol. The less soluble hexylerythrol crystallises in aggregates of colourless, lustrous, right-angled tables, melts at 95·5°, and is sparingly soluble in cold alcohol, almost insoluble in ether, and readily soluble in water; its taste is slight, but sweet and cooling. The more soluble hexylerythrol is very hygroscopic, and more soluble in alcohol and ether-alcohol than the preceding compounds; its taste is slight, but sweet and cooling.

The production of two isomeric hexylerythrols in this way renders it very probable that diallyl is not a homogeneous compound, but consists of two isomerides, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ and $CHMe{:}CH{\cdot}CH{:}CHMe$, and additional evidence in favour of this view is to be found in the results obtained by Sabanéeff (Abstr., 1885, 495) in brominating, and by Sorokin (Abstr., 1878, 962; 1880, 370) in oxidising the hydrocarbon.

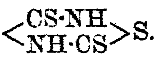
Neither diallyl dioxide nor its first hydrate could be detected among the oxidation products of diallyl, and inasmuch as Přibytek has shown that diallyl dioxide is not completely converted into the corresponding erythrol by heating with water at 100° for 40 hours (*Inaug. Diss., St. Petersburg*, 1887, 33), the author concludes that the hexylerythrols are obtained directly by the oxidation of diallyl without the formation of the corresponding oxides as intermediate products.

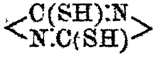
W. P. W.

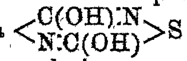
Hydration of Methylamylacetylene: Ethyl Amyl Ketone. By A. Béhal (*Bull. Soc. Chim.*, **50**, 359).—*Ethyl amyl ketone*, $C_8H_{16}O$, is obtained when the product of the hydration of methylamylacetylene is treated with sodium hydrogen sulphite, and kept for 10 days. The product is then pressed in a calico filter, the liquid which runs off, consisting of an aqueous and an oily layer, separated, and the oil washed, dried, and distilled. It boils at 164—166°, has a penetrating odour, is insoluble in water, and does not combine with hydrogen sodium sulphite. Sp. gr. = 0·8502 at 0°. N. H. M.

Preparation of Ethylene Cyanide. By A. Fauconnier (*Bull. Soc. Chim.*, **50**, 214).—Ethylene bromide (300 grams) and alcohol (500 grams) are boiled in a reflux apparatus and a saturated aqueous solution of potassium cyanide (200 grams) is gradually added. The reaction is completed in less than two hours, when the product is allowed to cool, and the liquid decanted, and evaporated in a vacuum. The residue is then dissolved in absolute alcohol, and the solution distilled first from a water-bath, then in a vacuum over a flame. It boils at 147° under 10 mm. pressure, and solidifies to a colourless mass, sometimes crystalline and sometimes amorphous. The yield is 75 to 80 per cent. of the theoretical. N. H. M.

Perthiocyanic and Dithiocyanic Acids. By P. Klason (*J. pr. Chem.* [2], **38**, 366—387. Compare Abstr., 1887, 1025).—The isoperthiocyanic acid prepared by mixing a solution of ammonium thiocyanate (1 kilo. in 650 c.c.) with hydrochloric acid (1 litre of 35—40 per cent.) contains 10—15 per cent. of dithiocyanic acid, even after fractional crystallisation from 60 per cent. acetic acid. The pure acid is best obtained by decomposing the barium salt with hydrochloric acid and recrystallising from a solution in 60 per cent. acetic acid. Isoperthiocyanic acid is very sparingly soluble in water, alcohol, and ether, but crystallises from acetic acid in beautful, yellow, dichroic prisms, which are the better formed the freer they are from dithiocyanic acid; its constitutional formula, according to Glutz, is

 $<\begin{array}{l}\mathrm{CS{\cdot}NH}\\ \mathrm{NH{\cdot}CS}\end{array}>\mathrm{S}$. When treated with alkalis, it is partially decomposed into dithiocyanic acid and sulphur; but a recombination takes place between some of the dithiocyanic acid, which is converted into the normal acid by the action of the alkali, and the sulphur, giving rise to a salt of normal perthiocyanic acid; thus the final result of the action of an alkali on isoperthiocyanic acid is a mixture of the alkaline salts of dithiocyanic acid and normal perthiocyanic acid.

Normal perthiocyanic acid is best prepared as follows:—100 grams of barium hydroxide, 50 grams of crude isoperthiocyanic acid, and 300 grams of water are gently warmed together until the sulphur at first separated has mostly redissolved. The mixture is then concentrated and cooled, when the barium perthiocyanate crystallises out, and is decolorised and recrystallised. If a fairly strong solution of this salt is mixed with hydrochloric acid, the iso-acid crystallises out; but if the solution is weak and is cooled to 0° nothing crystallises; if the cooled solution is shaken with ether, the normal acid is extracted and is obtained, together with some of the iso-acid, when the ethereal solution is evaporated at a low temperature. It is colourless and easily soluble in water and in ether; it easily passes into the iso-acid, and its constitution is probably expressed by the formula  $<\begin{array}{l}\mathrm{C(SH){:}N}\\ \mathrm{N{:}C(SH)}\end{array}>\mathrm{S}$, its properties indicating the presence of two SH-groups.

When a solution of iodine is added to a solution of a perthiocyanate, the colour of the former disappears, and a white precipitate is afterwards formed, but it is too unstable for analysis. Potassium permanganate is also bleached by a perthiocyanate, 1 mol. of the acid absorbing 8 atoms of oxygen; this would account for the oxidation of two of the sulphur-atoms to sulphuric acid and the formation of an acid of the formula  $<\begin{array}{l}\mathrm{C(OH){:}N}\\ \mathrm{N{:}C(OH)}\end{array}>\mathrm{S}$; but this has not been obtained in a state fit for analysis.

A solution of potassium perthiocyanate gives a green precipitate with copper sulphate, a yellow one with lead and bismuth salts, and a white one with silver nitrate—all insoluble in excess of the perthiocyanate; the precipitates formed with cadmium, zinc, mercury, cobalt, nickel, and ferrous salts are all soluble in excess of the perthiocyanate. Ferric chloride gives a black precipitate which gradually becomes white. *Barium perthiocyanate* crystallises in slender needles containing 4 mols. H_2O, three of which are lost at 110° and the fourth at 150°; it is easily soluble, forming an alkaline solution which is converted into barium thiocyanate and sulphur when heated for 12 hours on the water-bath. The *neutral* and *acid potassium* salts, the *calcium*, *lead*, and *silver* salts are also described. The *ethyl* salt, $Et_2C_2N_2S_3$, is a strongly refractive, colourless oil of the consistency of olive oil; its sp. gr. is 1·2544 at 18°; it has a faint, sweet smell, and boils in a vacuum at about 190°. When heated with strong hydrochloric acid, in which it is soluble, in a sealed tube, it is decomposed with formation of ammonia, carbonic anhydride, hydrogen sulphide, ethyl hydrosulphide, and ethyl polysulphide. Alcoholic potassium hydrosulphide converts it into ethyl hydrosulphide and potassium perthiocyanate. The ethyl and sulphur thus appear to be directly united.

Perthiocyanoglycollic acid, $C_2N_2S(S{\cdot}CH_2{\cdot}COOH)_2$, is obtained when isoperthiocyanic acid (1 mol.) is first shaken with a solution of potassium hydroxide (2 mols.) for some time, and a solution of sodium chloracetate (2 mols.) then added. This mixture is heated on the water-bath and hydrochloric acid added, when the free acid crystallises out on cooling in long, slender, obliquely cut, colourless tables. It melts with decomposition at 177°, and is nearly insoluble in cold, but easily soluble in hot water. Its solution gives white precipitates with lead acetate and silver nitrate, and a yellow one with ferric chloride. When heated with hydrochloric acid in a sealed tube, thioglycollic acid is formed among other products. The *potassium*, *barium* (with 3 mols. H_2O), *calcium* (with 3·5 mols. H_2O), *zinc*, *cadmium*, and *copper* salts are described. The *ethyl* salt cannot be distilled; the *amide* forms slender prisms which melt at 125°.

The dithiocyanic acids were first described by Fleischer; the iso-acid is always obtained along with isoperthiocyanic acid when a thiocyanate is decomposed by an acid; but the author has never obtained it in the pure state.

The normal dithiocyanates are colourless, not yellow, as Fleischer has stated; the author has not obtained them free from perthiocyanates, from which they differ in that with ferric chloride they give a dark-red coloration which rapidly changes to yellow and finally to a greyish-white precipitate. When it is attempted to prepare the ethyl salt, ethyl thiocyanate is obtained; nor can the hydrogen in the acid be displaced by any organic radicle without decomposing the molecule with formation of a thiocyanic derivative. A. G. B.

Platinum Compounds of Methyl Sulphide. By C. ENEBUSKE (*J. pr. Chem.*, [2], **38**, 358—365).—Three isomeric chlorides, of the general formula $PtCl_2,2Me_2S$, are obtained by the action of potassium platinosochloride on methyl sulphide. The *α-platosomethylsulphine chloride*, $Pt(SMe_2)_2Cl_2$, crystallises from chloroform in citron-yellow, transparent, monosymmetrical crystals melting at 159°; after melting, it dissolves in chloroform with formation of both the α- and β-chlorides. The *β-chloride* forms quadratic tables which contain 1 mol. of chloroform; it melts at 159°, and gives both chlorides after melting. A red, pulverulent chloride is first formed when potassium platinosochloride acts on methyl sulphide, and this becomes yellow and flocculent at a temperature of 50°; both forms are insoluble in chloroform, and are stable towards reagents; the author regards this as a double chloride of the formula $Pt(SMe_2Cl{\cdot}Cl{\cdot}Pt{\cdot}SMe_2{\cdot}SMe_2Cl)_2$. *Platosomethylsulphine bromide*, $Pt(SMe_2Br)_2$, forms bright yellow, monoclinic crystals; the *iodide* forms ruby-red crystals which decompose at 172°; the *sulphate*, $Pt(SMe_2O)_2SO_2 + 2H_2O$, forms yellowish crystals, easily soluble in water and melting at 91°; the *nitrate*, *nitrite*, *chromate* and *hydroxide* are also described.

The author has obtained salts of the radicle *platosomethyldisulphine*, $Pt(SMe_2)_4$.

The platinic derivatives are obtained from the platinous derivatives by treating their chloroform solutions with the halogens. *Platinomethylsulphine chloride*, $PtCl_2(SMe_2Cl)_2$, is a yellow, crystalline powder, decomposing at 218° without melting. The *bromochloride*, *bromide*, *iodochloride*, *iodobromide*, and *iodide* are also described.

A. G. B.

Action of Hot Manganese Dioxide on Alcohol Vapour. By E. DONATH (*Chem. Zeit.*, **12**, 1191—1192).—Carbonic anhydride, acetone, and small quantities of some higher boiling products are obtained when alcohol vapour is exposed to the action of manganese dioxide heated to temperatures varying from 150° to 360°, the latter being reduced to manganese sesquioxide, Mn_2O_3. Barium is frequently present as an impurity and in combination with the manganese, and such compounds give rise mainly to barium and manganese acetates, but also to salts of these metals with the higher homologous acids in small quantities. Mixing with lime did not increase the yield of acetic acid; but soaking the dioxide with sodium hydroxide and drying well was more successful in this respect. D. A. L.

Platinum Compounds of Ethyl Sulphide. By C. W. BLOMSTRAND (*J. pr. Chem.* [2], **38**, 352—358).—*α-Platosethylsulphine chloride*, $PtCl{\cdot}SEt_2{\cdot}SEt_2Cl$, is directly obtained by the action of potassium platinosochloride on ethyl sulphide. It melts at 81°. The crystals are bright yellow and monoclinic [$a : b : c = 1·5876 : 1 : 1·2610$; $\beta = 86°\ 4'$]. The *β-chloride*, $Pt(SEt_2Cl)_2$, is formed from the α-chloride and ethyl sulphide. It crystallises in greenish, monoclinic tables melting at 106° [$a : b : c = 1·5567 : 1 : 1·2961$; $\beta = 82°\ 44'$]. The *bromide*, $Pt(SEt_2Br)_2$, forms yellowish-red, monoclinic crystals melting at 118° [$a : b : c = 1·5072 : 1 : 0·98239$; $\beta = 87°\ 2·5'$]. The *iodide*, $Pt(SEt_2I)_2$, forms large, dark red, monoclinic crystals which melt at 136° [$a : b : c = 1·4714 : 1 : 0·9885$; $\beta = 89°\ 43'$].

Platosethylsulphine platinosochloride, $Pt(SEt_2Cl)_2,PtCl_2$, is obtained by heating platinous chloride for some time with ethyl sulphide (1 mol.); it is a yellow powder insoluble in alcohol.

Platosethylmethylsulphine chloride, $SEt_2Cl{\cdot}Pt{\cdot}SMe_2Cl$, is formed when platinous chloride acts on a mixture of ethyl and methyl sulphides; it is a heavy oil with a low freezing point. *Platosethylpropylsulphine chloride*, $SEt_2Cl{\cdot}Pt{\cdot}SPr_2Cl$, is a syrup which solidifies slowly; the *iodide* is precipitated by alcohol from a chloroform solution in small, lustrous, yellowish-red crystals.

Platosethylsulphine nitrite, $Pt(SEt_2{\cdot}O{\cdot}NO)_2$, is obtained by the action of fuming nitric acid on the sulphate (see below); it crystallises from chloroform in large, rhombic, pure white crystals which are sparingly soluble in cold water. The *sulphate* is formed from the chloride and silver sulphate; it is very soluble and crystallises in large, short, and thick crystals which have the formula $Pt(SEt_2O)_2SO_2 + 7H_2O$. The *phosphate*, *nitrate*, *chromate*, and *oxalate* have been obtained, and also, by treating the sulphate with barium hydroxide, a strongly alkaline solution of the *hydroxide*.

The platinic derivatives are obtained by dissolving the platinous derivatives (preferably in chloroform) and acting on the solution with the halogen. *Platinethylsulphine chloride*, $PtCl_2(SEt_2Cl)_2$, crystallises in small, bright-yellow tables and prisms which are triclinic, and melt with decomposition at 175°; the *bromide* forms red, monoclinic prisms: $\beta = 88° 30'$; the *bromochloride* forms yellowish-red crystals, and the *iodide* crystallises from chloroform in pretty dichroic prisms melting at 104°, dark-red by transmitted, and dark-blue by reflected light. A. G. B.

Oxidation of Unsaturated Compounds. By G. WAGNER (*Ber.*, **21**, 3347—3355; compare Abstr., 1888, 665).—When ethyl vinyl carbinol (b. p. = 114—114·5°) is oxidised with a dilute aqueous solution of potassium permanganate, it is converted into a series of compounds which can be partially separated by steam distillation. The neutral products volatile with steam, in addition to unaltered ethyl vinyl carbinol, consist of propaldehyde and a small quantity of a pungent substance distilling below 110°, which yields a reddish-brown oil containing nitrogen with phenylhydrazine, and is most probably ethyl vinyl ketone. The neutral product not volatile with steam (yield, 63 per cent. of that theoretically possible) is *pentenylglycerol*, $OH{\cdot}CHEt{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, a sweet, thick, and very hygroscopic syrup, which boils at 192° under 63·3 mm. pressure, has a sp. gr. = 1·0851 at 34° (water at 0° = 1), and is soluble in all proportions in water and alcohol, and also soluble to some extent in ether. Its *triacetate* is a syrup with a faint, alliaceous odour, boils at 177° under 52 mm. pressure, and at 264—265° under the ordinary pressure, has a sp. gr. = 1·122 at 0°, and = 1·103 at 18° (water at 0° = 1), and is soluble in the ordinary solvents. The acids volatile with steam consist of a mixture of formic and propionic acids, and the non-volatile acids comprise oxalic acid and a compound which, from the analysis of its zinc salt and behaviour with phenylhydrazine, is almost certainly propionylformic acid. To only a limited extent, therefore, under these conditions, is ethyl vinyl carbinol oxidised, as a secondary alcohol, to the corresponding ketone; on the contrary, it undergoes oxidation as though it were an olefine (Abstr., 1888, 665), yielding pentenylglycerol, which by further oxidation yields on the one hand, probably, propionic and oxalic acids, on the other formic and propionylformic acids, the last by its decomposition forming carbonic anhydride and propaldehyde.

Methyl allyl carbinol, when oxidised in like manner, yields as chief product (82 per cent. of that theoretically possible) *pentenylglycerol*, $OH{\cdot}CMeH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, which boils at 180° under 27 mm. pressure, has a sp. gr. = 1·135 at 0°, and = 1·120 at 22° (water at 0° = 1), is somewhat more mobile than its isomeride, and has a sweet but burning taste. Its *triacetate* has a cucumber-like odour, and a sp. gr. = 1·120 at 0°, and = 1·101 at 20° (water at 0° = 1). The neutral product volatile with steam is acetaldehyde, and the acids volatile with steam are formic and acetic acids, traces only of non-volatile acids being present. Inasmuch as no trace of a ketone could be found, methyl allyl carbinol under these conditions seems to be oxidised exclusively as an olefine.

Allyl alcohol, under like conditions, yields glycerol, acraldehyde and formic acid, and therefore forms oxidation products characteristic both of an olefine and of a primary alcohol.

Unsaturated aldehydes are known to yield the corresponding acids on oxidation, and hence behave like the saturated compounds. Unsaturated ketones, however, probably yield the corresponding hydroxyketones; thus, the production of hydroxyisobutyric and acetic acids by the oxidation of mesityl oxide (Pinner, Abstr., 1882, 941) is most probably preceded by the formation of the dihydroxyketone.

In the author's view, hydroxy-compounds are the primary oxidation-products of unsaturated hydrocarbons, alcohols and ketones when the oxidation is effected not only by dilute aqueous potassium permanganate but also by any substance which exerts a purely oxidising action, these primary products subsequently undergoing various further changes under the different conditions obtaining in each oxidation. The view hitherto generally accepted, that unsaturated compounds on oxidation break up at the point of the "double bonds," is no longer tenable even in those cases where decomposition is effected by fusion with potassium hydroxide, since this reaction finds its most probable explanation in the view that, for example, an acid, $CHR{:}CR'{\cdot}COOH$ (where $R = C_nH_{2n+1}$ and $R' = H$ or C_nH_{2n+1}) is first oxidised to the compound $CHR(OH){\cdot}CR'(OH){\cdot}COOH$, which then undergoes reduction to the β-ketonic acid $R{\cdot}CO{\cdot}CHR'{\cdot}COOH$, which in the presence of the alkali hydrolyses in the usual way into the acids $R{\cdot}COOH$ and $CH_2R'{\cdot}COOH$. W. P. W.

The Part played by Water in the Oxidation of Unsaturated Compounds. By G. WAGNER (*Ber.*, **21**, 3356—3360).—The author's experiments (Abstr., 1888, 665; preceding Abstract) show that unsaturated compounds when oxidised in the presence of water cannot combine directly either with oxygen or water, but invariably yield compounds formed by direct union with hydroxyl. Water, therefore, plays a very important part in the oxidation, and the reaction is probably represented, in the case of ethylene, by the equation $C_2H_4 + O + H_2O = C_2H_4(OH)_2$. Thermochemical data show that the formation of glycol by the oxidation of ethylene, according to this equation, involves the liberation of 58·4 cal., whereas the production of acetaldehyde by the action of oxygen on the hydrocarbon would require an absorption of 33 cal. W. P. W.

Preparation of Epichlorhydrin. By A. FAUCONNIER (*Bull. Soc. Chim.*, **50**, 212—214).—Dichlorhydrin is best obtained by the action of hydrogen chloride on glycerol at 120—130° (Abstr., 1888, 244). Water and acid with traces of the symmetrical dichlorhydrin (b. p. 176°) distil over. The product is distilled in a vacuum. The fraction boiling at 50—120° contains the two dichlorhydrins, and the fraction boiling at 120—150° the two monochlorhydrins. The monochlorhydrins with the addition of more glycerol, are again treated with hydrogen chloride. With 3 or 4 kilos. of glycerol, the operation takes 30 to 40 hours.

Epichlorhydrin is prepared by treating the crude dichlorhydrin with very strong potash or soda, following Reboul's method. The product is decanted and distilled in a vacuum; the epichlorhydrin distils over below 75°; the fraction boiling at 75—120° is unchanged dichlorhydrin. The crude epichlorhydrin is washed with water, and distilled without previously drying it; the fraction boiling at 116—118° is redistilled in a vacuum. The yield is very good, and with little trouble 1500 to 2000 grams can be prepared in a week. N. H. M.

Benzoic Acetals of Mannitol. By J. Meunier (*Compt. rend.*, **107**, 910—911; compare Abstr., 1888, 950).—The benzoic acetal of mannitol is very readily obtained by dissolving mannitol in sulphuric or hydrochloric acid, adding the requisite quantity of benzaldehyde, and agitating, when the mixture becomes completely solid. Pure mannitol is not necessary. The acetal is insoluble in water, acids, alkalis, and cold alcohol, &c., and hence is easily purified by washing. It is readily reconverted into mannitol and benzaldehyde, and hence may be utilised to separate mannitol from mixtures, such as plant juices, in which it occurs along with albuminoïds, glucose, &c.

When the benzoic acetal is perfectly free from benzaldehyde it resists the action of acids as well as alkalis, and is not decomposed even by prolonged boiling with acidified water. If, however, a small quantity of the aldehyde is present, the acetal is readily decomposed, the rate of decomposition increasing with the quantity of aldehyde. In fact, decomposition will take place when it is treated with sulphuric acid of only 1 per cent. C. H. B.

Sugar obtained from Plantago Psyllium. By R. W. Bauer (*Annalen*, **248**, 140—144).—The carbohydrate obtained from the epidermis of *Psyllium gallicum*, by boiling the aqueous extract with dilute sulphuric acid, is xylose. It was identified by its melting point, rotatory power, and by its compound with phenylhydrazine. W. C. W.

Amylene Nitrosate and its Derivatives. By O. Wallach (*Annalen*, **248**, 161–175).—Amylene nitrosate, $NO_2\cdot O\cdot CMe_2\cdot CMe{:}NOH$, is prepared by the action of nitric acid (sp. gr. 1·385) on a mixture of amyl nitrite, amylene, and glacial acetic acid. The best yield is obtained with an amylene boiling at 36—38°. The crude product decomposes in closed vessels, but is tolerably stable when exposed to the air. It is purified by recrystallisation from warm benzene, and afterwards from ethyl acetate; if the solvent is rapidly evaporated, the nitrosate is deposited in needles, but on slow evaporation fine monoclinic crystals resembling cubes in appearance are deposited; axial ratios, $a : b : c = 0·977 : 1 : 1·4485$; $\beta = 83° 32'$. By the action of potassium cyanide on amylene nitrosate (Abstr., 1888, 38), the nitrile, $CN\cdot CMe_2\cdot CMe{:}NOH$, is formed. This substance melts at 99—100°, and boils at 280° with partial decomposition. It is freely soluble in water, alcohol, ether, and benzene. On saponification, it yields an amide, $CONH_2\cdot CMe\cdot CMe{:}NOH$, and the hydroxylamine-derivative of dimethylacetic acid or *ketoximedimethylacetic acid*, $OH\cdot N{:}CMe\cdot CMe_2\cdot COOH$. The acid is freely soluble in alcohol, benzene, and water. The silver salt is deposited from aqueous or alcoholic solutions in needles. The acid melts at 96—97° with decomposition, yielding carbonic anhydride and the ketoxime of methyl isopropyl ketone, $CHMe_2{\cdot}CMe{:}NOH$. The synthesis of ketoximedimethylacetic acid from amylene nitrosate shows that this compound is derived from trimethylethylene.

Amylenenitrolpiperidide, $C_5NH_{10}{\cdot}CMe_2{\cdot}CMe{:}NOH$, is best prepared by the action of amylene nitrosate on an alcoholic solution of piperidine. It is deposited from alcohol in glistening prisms. By the action of boiling dilute sulphuric acid, it is converted into the *keto-base*, $C_5NH_{10}{\cdot}CMe_2{\cdot}COMe$, a colourless liquid boiling at 219—220°, sp. gr. 0·934. The hydrochloride is very hygroscopic, but the platinochloride, $(C_{10}H_{19}NO)_2,H_2PtCl_6$, forms fine crystals. W. C. W.

Aldehyde and Acetone Sulphites of Organic Bases. By H. Schiff (*Annalen*, **248**, 144—146).—Not only primary monamines but also secondary and tertiary amines and diamines have the power of uniting with aldehydosulphites to form crystalline compounds. W. C. W.

Sulphines. By G. Patein (*Bull. Soc. Chim.*, **50**, 201—206; compare Abstr., 1888, 664).—When the compound SEt_2Br_2, prepared by Cahours by the action of bromine on methyl sulphide, is dissolved in water (8 mols.), it is decomposed with liberation of hydrogen bromide. When the alcoholic solution is treated with zinc, the solution evaporated, and the viscous product dissolved in water and treated with mercuric chloride, the *compound* $SMe_2,HgCl_2 + SMe_2,ZnBr_2$ is obtained as a white precipitate.

The *iodide*, SMe_2I_2, prepared by the action of iodine on the sulphide, is crystalline and resembles iodine in appearance; it dissolves in alcohol, ether, and benzene, but not in water, and has an unpleasant odour. It is converted by anhydrous alcoholic ammonia into iodoform, and a compound of iodoform with methyl suphide. When treated with silver cyanide, silver iodide, cyanogen iodide and methyl sulphide are formed. N. H. M.

Symmetrical Dibromacetone. By E. Hjelt and V. O. Sivén (*Ber.*, **21**, 3288—3289).—Dibromacetone (symmetrical) can be prepared by oxidising dibromhydrin (50 grams) with a mixture of potassium dichromate (25 grams), sulphuric acid (40 grams), and water (40 grams), and purifying the product by means of the sodium hydrogen sulphite compound (compare Aschan, this vol., p. 31). The yield is 20—25 per cent. of the dibromhydrin employed. It is a colourless liquid with a pungent odour (compare Völker, Abstr., 1878, 781). The hydrogen sodium sulphite compound, $C_3H_4OBr_2,NaHSO_3 + 1\frac{1}{2}H_2O$, crystallises in nacreous plates and effloresces on exposure to the air. Dibromacetone yields a very unstable compound, $C_3H_4OBr_2,NH_3$, with ammonia, and it also reacts with phenylhydrazine. The *oxime* crystallises in slender needles. When the acetone is heated with Fehling's solution, the latter is reduced, and when it is dissolved in baryta-water or potassium carbonate, solutions are obtained which probably contain dehydroxyacetone, as they reduce Fehling's solution when warmed with it, and yield a syrupy liquid when evaporated and extracted with alcohol. F. S. K.

Preparation of Ketones. By J. HAMONET (*Bull. Soc. Chim.*, **50**, 355—358).—*Propione*, $COEt_2$, is prepared by digesting propionic chloride (1 mol.) with ferric chloride (1 mol.), using a reflux apparatus. The mixture is at first cooled and afterwards heated at about 60°. The product is poured into a little well-cooled water and the oil washed with water and distilled. It boils at 101—102°. The yield is about 34 per cent. of the theoretical.

Butyrone, $COPr_2$, is obtained by heating butyric chloride (4 mols.) and ferric chloride (1 mol.) at 45° or 50°; the black oil is washed with alkaline water before being distilled. It is lighter than water, and boils at 142—144°.

Œnanthylone was prepared from heptylic chloride. N. H. M.

Diethoxyacetone. By E. GRIMAUX and L. LEFÈVRE (*Compt. rend.*, **107**, 914—916).—Ethyl ethoxyaceto-ethoxyacetate is allowed to remain 48 to 72 hours at the ordinary temperature with a sufficient quantity of a 2·5 per cent. solution of potassium hydroxide to convert it into the potassium salt. The liquid is then acidified with sulphuric acid which liberates the free acid, and the latter at once decomposes with evolution of carbonic anhydride. The liquid is extracted with ether and the ethereal solution dried and distilled. The greater part of the residue boils at 193—196°, and the yield is 20—25 per cent. of the original ethereal salt.

Diethoxyacetone, $CO(CH_2{\cdot}OEt)_2$, boils at 195°, and is a colourless liquid with an aromatic odour and a sweet, burning taste; sp. gr. at 17·8° = 0·980; vapour-density 4·95. It dissolves in alcohol and ether, and is slightly soluble in water; it volatilises in steam. Diethoxyacetone combines with sodium hydrogen sulphite with great development of heat, forming a very soluble compound. Its reducing power is very much greater than that of an equal weight of glucose. It readily reduces Fehling's solution, and yields a mirror with ammoniacal silver nitrate even at the ordinary temperature.

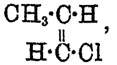
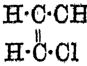
It cannot be converted into symmetrical dichloracetone. When treated with sodium ethoxide, an energetic reaction takes place with formation of brown, resinous products, insoluble in water but soluble in alkalis.

Diethoxyacetone is remarkable in having the properties of both ketones and ethereal derivatives of glycols. C. H. B.

Action of Copper Acetylacetone on Carbonyl Chloride. By THOMAS and LEFÈVRE (*Bull. Soc. Chim.*, **50**, 193—194).—When the powdered copper-derivative is heated at 60—70° with carbonyl chloride dissolved in benzene, the product filtered and evaporated, crystals are obtained which are recrystallised from ether. The new compound melts at 120—121°. When heated, a sublimate of large, yellow needles is obtained which seems to be a different substance. It dissolves in alcohol, ether, and benzene, very readily in chloroform; warm water seems to decompose it. When heated with ammonia, it dissolves at once and yields a compound melting at 250°. The composition of the compounds has not yet been determined.

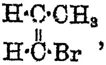
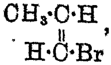
N. H. M.

Arrangement of Atoms in Space. Geometrical Constitution of the Crotonic Acids and their Halogen Substitution Products. By J. WISLICENUS and, in part, E. TEISLER and H. LANGBEIN (*Annalen*, **248**, 281—355).—α-β-Dichlorobutyric acid and its derivatives have already been described by the author (Abstr., 1887, 655). α-β-Isodichlorobutyric acid is prepared by saturating a mixture of isocrotonic acid and carbon bisulphide with chlorine. After removing the solvent by passing a current of dry air through the product, a small quantity of α-β-dichlorobutyric acid is deposited in crystals, but the α-β-isodichlorobutyric acid remains as a non-crystallisable oil. α-β-Isodichlorobutyric acid yields α-chlorocrotonic acid when it is treated with an excess of an aqueous solution of sodium hydroxide, and an aqueous solution of its sodium salt decomposes at 80°, yielding carbonic anhydride and α-chloropropylene (b. p. 36°).

α-Isochloropropylene,  $\begin{array}{c}CH_3\cdot C\cdot H\\ \Vert\\ H\cdot C\cdot Cl\end{array}$, is easily attacked by alkalis at 100° and converted into allylene. α-Chloropropylene,  $\begin{array}{c}H\cdot C\cdot CH_3\\ \Vert\\ H\cdot C\cdot Cl\end{array}$, is less readily attacked.

In the preparation of α-β-dichlorobutyric acid by the action of chlorine on a solution of solid crotonic acid in carbon bisulphide, an oily bye-product is obtained It consists of a mixture of α-β-isodichlorobutyric acid with the normal isomeride. The amount of this bye-product is increased by raising the temperature at which the reaction takes place.

The chief product of the action of bromine on isocrotonic acid mixed with carbon bisulphide is α-β-isodibromobutyric acid. A small quantity of solid α-β-bromocrotonic acid is also formed. α-β-Isodibromobutyric acid is decomposed by an excess of alkali, yielding at the ordinary temperature α-bromocrotonic acid, but at 100° a mixture of α-isobromopropylene (b. p. 59—60°) and a new α-bromopropylene (b. p. 63—64°). The latter is more conveniently prepared by converting α-isobromopropylene (from α-β-dibromobutyric acid) into tribromopropane by the action of bromine. The ααβ-tribromopropane is mixed with alcohol and treated with zinc-dust.

α-Bromopropylene,  $\begin{array}{c}H\cdot C\cdot CH_3\\ \Vert\\ H\cdot C\cdot Br\end{array}$, is not easily attacked by alkalis, but α-isobromopropylene,  $\begin{array}{c}CH_3\cdot C\cdot H\\ \Vert\\ H\cdot C\cdot Br\end{array}$, is converted into allylene.

One part of potassium bromocrotonate dissolves in 493·4 parts of 99·5 per cent. alcohol at 21°. Under similar conditions, potassium isobromocrotonate only requires 10·8 parts of alcohol.

αβ-Dichlorobutyric acid is partly converted into αβ-isodichlorobutyric acid by exposure to a temperature of 100—185°, and chloro- and bromo-crotonic acids are always formed in small quantities when αβ-isochloro- or bromo-crotonic acids are distilled in a current of steam. Exposure to a small quantity of hydrogen chloride at 100° partially converts isocrotonic into crotonic acid.

α-Isobromocrotonic acid is completely converted into crotonic acid by the action of sodium amalgam in alkaline solution, but in an acid solution isocrotonic acid is formed as well as crotonic acid.

The author concludes by replying to the criticisms of Michael (Abstr., 1888, 1147 and 1176). W. C. W.

Action of Phosphorus Sulphides on Dibromosuccinic Acids. By I. Ossipoff (*J. Russ. Chem. Soc.*, 1880, **20**, 245—254).—If, as is generally admitted, dibromosuccinic acid is a derivative of fumaric acid and isodibromosuccinic acid of maleïc acid, the first ought to be convertible into thiophen or its derivatives. The author finds, however, that dibromosuccinic acid, when heated with phosphorus trisulphide or pentasulphide under the ordinary pressure at 140°, does not give a thiophen compound. In sealed tubes with phosphorus trisulphide, nothing but thiomalic acid was formed. No better result was obtained when the sodium salt of dibromosuccinic acid was employed or with isodibromosuccinic acid or its anhydride. These results are not in accordance with the equations Kues and Paal give (*Ber.*, **19**, 555) as representing the formation of thiophen. B. B.

The Ethereal Salts of Fumaric and Maleïc Acids. By I. Ossipoff (*J. Russ. Chem. Soc.*, 1888, **20**, 254—267).—Silver fumarate was treated with isobutyl iodide in the presence of ethyl ether, but hardly any reaction took place. Silver maleate with isobutyl or isoamyl bromide gave no better results; the same is the case with the iodides of higher alcohol radicles.

Ethyl and isopropyl maleates were found to have a normal vapour-density. The same is the case with isopropyl fumarate, but the isobutyl salt is found to decompose under these circumstances; even isopropyl fumarate, which shows the normal vapour-density at the boiling point of amyl benzoate, decomposes at the boiling point of β-naphthol (285—290°).

The mono-silver salt of maleïc acid (acid silver maleate) gave, with ethyl iodide, hydrogen ethyl maleate, and from this the sodium salt, $C_4H_2O_4EtNa$, was obtained. This, after decomposition with sulphuric acid, gives free ethylmaleïc acid, which is not identical with ethylfumaric acid.

With acetic chloride, the above sodium salt gives a compound which would seem to be the acetyl-derivative of ethylmaleïc acid, as when it is treated with ethyl alcohol at the ordinary temperature it yields ethyl acetate and ethyl maleate. When maleïc anhydride is heated in a sealed tube with benzyl alcohol, a mixture of substances is obtained consisting chiefly of sodium benzylmaleate. Phenol gives no reaction with maleïc anhydride. B. B.

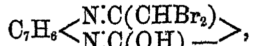
Compounds of Dibromopyruvic Acid with Hydrazines. By O. Nastvogel (*Annalen*, **248**, 85—92).—*Phenylosazonglyoxalcarboxylic acid*, $N_2HPh{:}CH{:}C(N_2HPh)\cdot COOH$, is deposited in orange-coloured crystals on mixing aqueous solutions of phenylhydrazine and dibromopyruvic acid. It melts at 201—203° with decomposition, and is soluble in acetone, acetic acid, and in boiling alcohol or benzene. The sodium, potassium, and ammonium salts are crystalline, and are sparingly soluble in water.

Paratolylosazoneglyoxalcarboxylic acid, $C_{17}H_{18}N_4O_2$, melts at 186—188° with decomposition, and dissolves freely in warm alcohol, acetone, benzene, and acetic acid. The sodium, potassium, and ammonium salts are much more soluble in hot than in cold water.

α-Naphthylosazoneglyoxalcarboxylic acid forms cherry-red crystals and melts at 196°. β-Naphthylhydrazine and dibromopyruvic acid unite together, forming a hydrazide, probably

$$C_{10}H_7{\cdot}N_2H{:}CH{\cdot}CO{\cdot}C(OH){:}N_2H{\cdot}C_{10}H_7.$$

This substance is insoluble in alkalis, and is decomposed by boiling with an alcoholic solution of potassium hydroxide.

Dibromomethylhydroxytoluquinoxaline,  $C_7H_6{<}\substack{N{:}C(CHBr_2)\\ N{:}C(OH)\,—}{>}$, is formed when a mixture of orthotoluylenediamine and dibromopyruvic acid in molecular proportions is boiled. It melts with decomposition at 235°, and is reprecipitated on adding an acid to its solution in alkalis. W. C. W.

Tricarballylic Acid. By P. DÄUMICHEN (*Chem. Centr.*, 1888, 1347—1348).—In the preparation of ethyl malonate from monochloracetic acid and potassium cyanide, an oil of high boiling point (286—287°) was obtained as a bye-product. Its behaviour with barium hydroxide and hydrochloric acid, its elementary analysis and the analysis of its silver and copper salts, showed it to consist of triethyl tricarballylate.

No well-characterised substance is obtained from tricarballylic acid by subjecting it to distillation.

Benzyl tricarballylate, prepared from the sodium salt and benzyl chloride, consists of lustrous, pearly leaves, soluble in alcohol, sparingly in ether, insoluble in water. It may be prepared more readily by neutralising the alcoholic solution of tricarballylic acid with potash, distilling off the greater portion of the alcohol, and boiling with benzyl chloride in a reflux apparatus. *Acetyl tricarballylic anhydride*, $C_{18}H_{14}O_{11}$, prepared by boiling carballylic acid with excess of acetic chloride, melts at 128—129°; when exposed to moist air, it becomes hydrated, with formation of acetyl tricarballylic acid. *Tricarballylanilic acid*, $C_{12}H_{11}NO_4$, prepared by heating 1 gram of tricarballylic acid with 3·18 grams of aniline, forms lustrous, pearly scales, and melts at 137°. *Tricarballylparatoluic acid* crystallises with 1 mol. H_2O and melts at 174°. These two acids take up water when dissolved in it, and pass into the bibasic derivatives; their silver salts are amorphous, as also the copper salts of the toluyl-derivative. The *tricarballylparaditoluic acid* was also obtained; it melts at 174°, is monobasic, and, with the heavy metals, forms salts which are amorphous. *Tricarballylparatoluidide* was also found as a product of the action of toluidine on tricarballylic acid; it melts at 253°. *Tricarballylparaditoluyl* is formed by dissolving paratoluidine and tricarballylic acid in alcohol; it melts at 178°, and when boiled with alkalis passes into the paraditoluic acid.

Tricarballylamide is prepared by treating ammonium tricarballylate in ammoniacal solution in a sealed tube, or by protracted agitation of the triethyl salt with ammonia; it melts at 218° with decomposition, ammonia being evolved, and *tricarballylamideimide* remains; this melts at 172—173°. J. W. L.

Rate of Oxidation of Tartaric Acid. By J. KRUTWIG (*Zeit. physikal. Chem.*, **2**, 787—795).—The author doubts the generality of the conclusions arrived at by Dreyfus (Abstr., 1888, 24), and gives the details of an investigation on the oxidation of tartaric acid by means of potassium permanganate under different conditions. He shows that the rate of oxidation increases with the amount of tartaric acid present, and that it also proceeds more rapidly without than with the addition of sulphuric acid. The reaction takes place much more readily in sunlight than in the dark, and the addition of excess of sulphuric acid up to a certain point has an accelerating influence, as has also the presence of manganese sulphate in the solution. H. C.

Alloxan Sulphites of Organic Bases. By G. PELLIZARRI (*Annalen*, **248**, 146—152).—The following compounds were prepared by adding an aqueous solution of alloxan to solutions of organic sulphites saturated with sulphurous anhydride:—*Alloxan ethylamine sulphite*, $C_2H_7N,SO_3H_2,C_4H_2N_2O_4 + H_2O$, forms colourless, monoclinic crystals; $a : b : c = 0·8341 : 1 : 1·2462$; $\beta = 100° 40' 20''$. *Alloxan aniline sulphite*, $C_6H_7N,SO_3H_2,C_4H_2N_2O_4 + 2H_2O$, crystallises in large, quadratic plates. The methylaniline compound, $C_7H_9N,SO_3H_2,C_4H_2N_2O_4 + 2H_2O$, forms small, yellowish prisms. *Alloxan dimethylaniline sulphite*, $C_8H_{11}N,SO_3H_2,C_4H_2N_2O_4 + 4H_2O$, forms monoclinic plates; $a ; b : c = 1·3399 : 1 : 0·3394$; $\beta = 99° 22' 40''$. The benzidine compound forms triclinic prisms containing 1 mol. H_2O. Tolidine and amidobenzoic and aspartic acids yield similar compounds. *Alloxan pyridine sulphite* is triclinic. The crystals are anhydrous. Anhydrous crystalline compounds are also obtained with quinoline, picoline, morphine, and cinchonine. The strychnine compound crystallises with 1 mol. H_2O, and the brucine compound with $1\frac{1}{2}$ mol. H_2O. *Alloxan ammonium sulphite* forms triclinic crystals; $a : b : c = 0·6648 : 1 : 0·7121$; $\alpha = 71° 11' 20''$, $\beta = 99° 47' 20''$, and $\gamma = 80° 40'$. The aqueous solution decomposes on boiling, forming a small quantity of murexide; in presence of ammonia or ammonium carbonate, ammonium thionurate is produced. W. C. W.

Glycocine-derivative of α-Thiophenic Acid. By M. JAFFÉ and H. LEVY (*Ber.*, **21**, 3458—3461).—α-Thiophenic acid is not poisonous, and can be given to rabbits in the form of sodium salt in daily quantities of 2 grams by subcutaneous injection. It is excreted in the urine as α-thiophenuric acid, the glycocine-derivative of α-thiophenic acid.

α-Thiophenuric acid, $C_7H_7NSO_3$, crystallises from water in colourless, transparent, strongly refractive, thin prisms, closely resembling those of hippuric acid, melts at 171—172°, and is very sparingly soluble in ether, but readily soluble in alcohol and hot water. When boiled with baryta-water, it hydrolyses almost quantitatively into α-thiophenic acid and glycocine, but when hydrolysed with hydrochloric acid, it yields only small quantities of α-thiophenic acid, although the yield of glycocine is quantitative. The *silver* salt, $C_7H_6NSO_3Ag$, crystallises in colourless, microscopic needles, dissolves sparingly in water, and is unaffected by exposure to light; the *barium* salt (2 mols. H_2O) crystallises in colourless, slender needles, and is readily soluble in water, but insoluble in alcohol; the *calcium* salt (? 5 mols. H_2O) crystallises in thick, prismatic needles, and is extremely soluble in water.

W. P. W.

Influence of Light on the Action of Halogens on Aromatic Compounds. By J. SCHRAMM (*Monatsh.*, **9**, 842—853).—The present work, a continuation of the author's investigations (Abstr., 1885, 451), was conducted with the object of ascertaining the behaviour towards the halogens of aromatic compounds containing side-chains which are not normal.

Isopropylbenzene.—In the dark or in presence of iodine, bromine enters the benzene nucleus, a small quantity in the first case also displacing hydrogen in the side-chain. The product boils at 217—219° under a pressure of 739 mm., and on oxidation yields a mixture of para- and ortho-brombenzoic acids, chiefly the former. In direct sunlight, bromine (1 mol.) acts rapidly, the product being a clear liquid which solidifies at —20°. On distillation, this gives off large quantities of hydrogen bromide and about one-half of the original isopropylbenzene is recovered. It appears in this latter case that substitution in the side-chain takes place, a dibromisopropylbenzene being formed, which decomposes on distillation.

Isobutylbenzene.—In the dark or in presence of iodine, bromine enters the benzene nucleus, a *bromisobutylbenzene* being formed, which boils at 232·5—233·5° under a pressure of 739 mm., and solidifies at —18°. On oxidation, it yields parabrombenzoic acid. In direct sunlight, bromine reacts to form a compound which on distillation loses hydrogen bromide and yields a hydrocarbon boiling at 180—185°. This latter combines with bromine to form an oily bromide, but in other respects does not resemble Perkin's isobutenylbenzene.

Secondary butylbenzene, when treated with bromine in the dark or in presence of iodine, gives a *bromobutylbenzene* boiling at 235·5—237°. It is not readily oxidised, but yields parabrombenzoic acid when heated for seven days with a concentrated solution of alkaline permanganate. The action of bromine in sunlight is rapid, but the product was not examined.

By the action of bromine in the dark or in presence of iodine, tertiary butylbenzene (trimethylphenylmethane) is converted into a *bromobutylbenzene* boiling at 230—230·5° under a pressure of 736 mm., and of sp. gr. 1·2572. This compound cannot be oxidised unless with dichromate and excess of sulphuric acid, when it is destroyed. It is a remarkable thing that tertiary butylbenzene is not attacked by bromine in sunlight even when the solution is heated to the boiling point. As substitution of bromine in the side-chain always takes place with elimination of the hydrogen-atom attached to the carbon nearest the benzene nucleus, the absence of such a hydrogen-atom in tertiary butylbenzene may perhaps explain this behaviour.

In the dark or in presence of iodine, isoamylbenzene yields with bromine a *bromisoamylbenzene*, boiling at 253—255° under a pressure of 736 mm., and of sp. gr. 1·2144. On oxidation, it gives parabrombenzoic acid. Isoamylbenzene is readily acted on by bromine in direct sunlight, the product being a liquid *bromisoamylbenzene* which decomposes on distillation into hydrogen bromide and phenylisoamylene. Treated with another molecular proportion of bromine in the dark, it yields a *dibromisoamylbenzene* melting at 128—129°.

It appears from the author's researches that the action of halogens on aromatic hydrocarbons, in the dark and in direct sunlight, may be compared in its results to action at low and at high temperatures. By the first, substitution in the benzene nucleus takes place with formation of an ortho- or para-bromo-derivative, whereas by the second, substitution in the side-chain is effected. H. C.

Aromatic Cyanates and their Polymerides. By W. Frentzel (*Chem. Centr.*, 1888, 1361—1362).—*Ethyl pseudocumylcarbamate*, prepared from pseudocumidine and ethyl chlorocarbonate, dissolves readily in alcohol, and melts at 91·5°. Phosphoric anhydride eliminates 1 mol. H_2O from it with formation of *pseudocumylcyanate*, boiling at 221°. Triethylphosphine and, more readily, potassium acetate, change the cyanate into its polymeride, the *cyanurate* melting at 234°. *Dicumylcarbamide*, prepared from the cyanate, melts at 260—270°.

From unsymmetrical metaxylidine [$Me_2 : NH_2 = 1 : 3 : 4$], the *carbamate*, melting at 57°, and from this the *cyanate*, boiling at 205°, were prepared, and by means of potassium acetate, the *cyanurate* melting at 162° was obtained.

From the symmetrical metaxylidine [$Me_2 : NH_2 = 1 : 3 : 5$], the *carbamate* melting at 77·5°, the *cyanate* boiling at 208·5°, and, by means of carbonyl chloride, *dixylylcarbamide* melting at 275° were prepared. *Monoxylylcarbamide*, melting at 162°, was prepared from the last-mentioned compound by evaporating the aqueous solution of the hydrochloride with potassium cyanate. J. W. L.

New General Method for the Synthesis of Aromatic Compounds. By C. Friedel and J. M. Crafts (*Ann. Chim. Phys.* [6], 14, 433—472).—When dry air or oxygen is passed into cold benzene in presence of aluminium chloride, a very small quantity of phenol is formed, but when the mixture is heated almost to its boiling point this compound is produced in much larger quantities. After passing the gas, for some time, the mixture is poured into water, the supernatant oil separated and the phenol obtained in a perfectly pure state by extracting the acidified, aqueous solution with ether and evaporating. The oily product contains unaltered benzene and red compounds; the latter are soluble in ether, benzene, and carbon bisulphide, but insoluble in alcohol, acetic acid, and water, and cannot be distilled.

Metacresol can be obtained from toluene in like manner. In this reaction also oily bye-products are formed; these compounds are brown, soluble in toluene and cannot be distilled.

When benzene and powdered sulphur are heated together at 75—80°

in presence of aluminium chloride until the evolution of hydrogen chloride and hydrogen sulphide ceases, the mixture poured into water and the supernatant oil fractionated, the following compounds, together with unaltered benzene, are obtained: (1) Phenyl mercaptan boiling at 170—173°; (2) phenyl sulphide boiling at about 288°; and (3) diphenylene disulphide boiling at 364—366° (compare Stenhouse, *Annalen*, **149**, 252, and Graebe, this Journal, 1874, 469). A compound, $C_{12}H_8S_2O_2$, is obtained when diphenylene disulphide (1 mol.) is oxidised with chromic acid (1⅓ mol.) in glacial acetic acid solution (compare Graebe, *loc. cit.*). It crystallises from benzene in small prisms, melts at 241°, is readily soluble in glacial acetic acid, sparingly in cold benzene, and dissolves in concentrated sulphuric acid with a violet-red coloration.

Benzoic acid is produced, with evolution of hydrogen chloride, when a stream of dry carbonic anhydride is passed for some days through a mixture of benzene and aluminium chloride heated almost to its boiling point.

Phenylsulphinic acid is obtained by passing sulphurous anhydride into a warm mixture of benzene and aluminium chloride until the weight of the hydrogen chloride evolved is about half that of the aluminium chloride employed, and then gradually pouring the whole into cold water. If the reaction is continued too long or if the mixture is allowed to cool, a crystalline aluminium salt separates. The filtered aqueous solution is acidified with hydrochloric acid and the product extracted with ether.

When aluminium chloride is gradually added to a warm mixture of benzene and phthalic anhydride, hydrogen chloride is evolved and orthobenzoylbenzoic acid is formed.

Paratoluoylorthobenzoic acid, $C_6H_4Me{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is obtained when aluminium chloride (1½ parts) is added in small portions at a time to a mixture of phthalic anhydride (½ part) and toluene (1 part). The whole is then poured into a large quantity of water and, after keeping for some time, the crystalline product is separated. Further quantities can be obtained by evaporating the toluene. It crystallises from boiling toluene in white prisms, melts at 146°, is very readily soluble in benzene and alcohol, more sparingly in ether, and very sparingly in boiling water. Dilute aqueous solutions of the acid and solutions of many of its salts have a sweet taste. The *ammonium* salt crystallises from boiling water, in which it is very readily soluble, in silky needles. The *sodium* salt crystallises in small needles and is very readily soluble in water but more sparingly in alcohol. When heated with soda at about 340° it is decomposed almost quantitatively into sodium benzoate and sodium paratoluate. The *barium* salt (+ 4 mols. H_2O) crystallises from water in prisms or needles and loses its water at 110°. Most of the salts of the heavy metals are sparingly soluble in water.

Orthoduroylbenzoic acid, $C_6HMe_4{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, obtained in like manner, crystallises from glacial acetic acid in plates, melts above 260°, and is readily soluble in alcohol, ether, acetone, benzene, and toluene, but insoluble in water. The *potassium* salt crystallises in microscopic needles and is readily soluble in cold water. The *sodium* salt is sparingly soluble in alcohol and separates from the solution again only partially, in the form of small plates. The *ammonium* salt crystallises in needles. The *barium* salt (+ 1 mol. H_2O) crystallises in slender needles and is moderately soluble in alcohol but sparingly in water. The *calcium* salt (+ 1 mol. H_2O) crystallises from water in needles. The lead, silver, and copper salts are insoluble in water.

Acetophenone is formed when benzene is treated with acetic anhydride in presence of aluminium chloride.

When pure, dry ethylene is passed into a mixture of benzene and aluminium chloride heated at about 70—90°, ethyl-, diethyl- and triethylbenzene are produced, together with other higher boiling compounds.

Aluminium phenyl is formed when mercury phenyl is heated with aluminium foil at 125—130°. This compound will be fully described in a subsequent paper. It melts at about 230° and absorbs moisture with great avidity, but only absorbs oxygen very slowly when exposed to dry air. It yields diphenylmethane when treated with benzyl chloride, but it does not react with chlorobenzene at 100° in benzene solution. Phenol is formed when oxygen is passed through a benzene solution of aluminium phenyl, and when a xylene solution is heated with sulphur, diphenylene disulphide, phenyl sulphide, and probably also phenyl mercaptan are produced. These results show that aluminium phenyl behaves like a mixture of benzene and aluminium chloride, and the authors consider that this fact is evidence in favour of the view that an organo-metallic compound, probably $C_6H_5{\cdot}Al_2Cl_5$, is temporarily formed in all reactions; similar to those described above and those already described (*Ann. Chim. Phys.* [6], 1, 449), in which aluminium chloride is employed.

Gustavson (Abstr., 1885, 363) considers that the brown liquid, which is formed when aromatic hydrocarbons are placed in contact with aluminium chloride or bromide, has a definite composition, which, in the case of benzene, is $AlCl_3(C_6H_6)_3$ or $AlBr_3(C_6H_6)_3$, and that it is this compound which reacts with the chloride, bromide, or iodide of the alcohol radicle. The authors find that when pure aluminium chloride or bromide is mixed with dry benzene or toluene this liquid is not formed or only produced in very small quantities, and that in the case of aluminium chloride a considerable quantity remains undissolved in presence of excess of the hydrocarbon. When hydrogen chloride or bromide is passed into the mixture, as recommended by Gustavson, it was observed that the liquid was formed in some cases but not in others; when, however, a small quantity of water was admitted, the liquid was always produced. Analyses of the liquid obtained in various experiments showed that it was a complex mixture, perhaps consisting of a compound of the hydrocarbon with aluminium chloride, or more probably with a chlorhydroxide of aluminium, the organo-metallic compound $C_6H_5{\cdot}Al_2Cl_5$, excess of the hydrocarbon, and hydrochloric acid. F. S. K.

Influence of the Presence of Halogens and Alkyl-groups on the Replacement of Oxygen in Quinone-derivatives by the Isonitroso-group. By F. KEHRMANN (*Ber.*, 21, 3315—3321).—

Chloroquinone melting at 54° and bromoquinone melting at 55—56° react with hydroxylamine hydrochloride in alcoholic solution at the ordinary temperature. The monoximes obtained have the constitution $[NOH:X:O = 1:3:4]$, and are unstable, decomposing when heated for a long time at 80—90°. They are not easily obtained in the pure state, crystallise in small, bright-yellow needles, and are very readily soluble in alcohol and ether, but only moderately so in hot water, and very sparingly in boiling benzene, light petroleum, acetone, and carbon bisulphide. When reduced with tin and hydrochloric acid, they yield halogen amidophenols $[NH_2:X:OH = 1:3:4]$, and when treated with cold, concentrated nitric acid, they are converted into orthochloroparoximidoquinone decomposing at 140°, and orthobromoparoximidoquinone decomposing at 142° respectively. They are with difficulty converted into halogen dioximes $[(NOH)_2:X = 1:4:3]$ when boiled for a long time with excess of hydroxylamine hydrochloride in aqueous solution.

The dioximes crystallise in small, greyish-yellow needles, are sparingly soluble in boiling water, alcohol, and ether, moderately so in benzene, and are converted into halogen dinitroso-derivatives when oxidised with alkaline potassium ferricyanide solution or warm dilute nitric acid.

The halogen dinitroso-derivatives are yellow, crystalline compounds with a smell resembling both that of quinone and iodoform. They are readily volatile with steam, and dissolve in fuming nitric acid, from which they are precipitated unchanged on adding water, but are only very sparingly soluble in ordinary solvents. They yield diamines which are readily oxidised to quinones when treated with chromic acid or ferric chloride.

Metadichloroquinone melting at 120—121°, metadibromoquinone melting at 130—131°, and metadi-iodoquinone melting at 179° $[O_2:X_2 = 1:4:2:6]$ do not form dioximes. The monoximes are yellow, crystalline compounds, and are readily soluble in alkalis, alcohol, and ether, but sparingly in boiling water, benzene, and carbon bisulphide. The chloro-derivative decomposes at 140°, the bromo-derivative at 145°. These oximes are readily converted into metadihalogenparanitrophenols when treated with cold, moderately concentrated nitric acid (compare Fischer and Hepp, Abstr., 1888, 456). Their constitution is, therefore $[O:NOH:X_2 = 1:4:2:6]$.

Paradichloroquinone (m. p. 161—162°), parachlorobromoquinone (m. p. 171—172°), and paradibromoquinone (m. p. 188—189°) $[O_2:X_2 = 1:4:2:5]$, react with hydroxylamine hydrochloride under the conditions described above, forming both monoximes and dioximes which can be separated by means of alcohol or benzene.

Paradichloroparoximidoquinone crystallises in bright yellow needles, decomposes without melting when heated at 138°, and is readily soluble in alcohol and ether, but only sparingly in hot water, benzene, and carbon bisulphide. It is slightly volatile with steam, but resinifies when boiled for a long time with water.

Paradichloroparanitrophenol, $[OH:Cl_2:NO_2 = 1:2:5:4]$, obtained by dissolving the oximidoquinone in well-cooled, concentrated nitric acid, crystallises from hot water or dilute alcohol in colourless needles, and from absolute alcohol in short, thick, quadratic prisms melting at 115—116°. It does not taste bitter, and is somewhat volatile with steam. It yields an *amine* which is converted into paradichloroquinone melting at 161—162° when oxidised with ferric chloride.

Paradichloroquinonedioxime separates from benzene in greyish-yellow, granular crystals, and is readily soluble in boiling benzene, but sparingly in alcohol and ether, and insoluble in boiling water.

Paradichloroparadinitrosobenzene, prepared by dissolving the dioxime in fuming nitric acid, crystallises in citron-yellow needles, explodes when heated at 120—130°, and is insoluble in the ordinary solvents. It is not oxidised when boiled with nitric acid. The *amine*, obtained by reducing the dioxime or the dinitroso-compound, is converted into paradichloroquinone when treated with ferric chloride.

Trichloroquinone and tribromoquinone yield dark brown resinous products when treated with hydroxylamine hydrochloride in alcoholic solution, and no crystalline compound except tetrachloroquinol was obtained.

Chloranil and bromanil are gradually reduced to the corresponding quinols when boiled with hydroxylamine hydrochloride in alcoholic solution.

Trichlorotoluquinone, tribromotoluquinone, metadichlorometaxyloquinone, $[O_2 : Me_2 : Cl_2 = 1 : 4 : 2 : 6 : 3 : 5]$, dichlorothymoquinone, $\beta\beta$-dichloro- and dibromo-α-naphthaquinone do not combine with hydroxylamine under the conditions described above. It seems, therefore, that the quinone-derivative cannot yield an oxime when the hydrogen adjacent to the CO-group is displaced by halogens or alkyls.

Parachlorotoluquinone yields both a monoxime and a dioxime, but bromotoluquinone, $[O_2 : Me : Br = 1 : 4 : 2 : 6]$, and dibromotoluquinone, $[O_2 : Me : Br_2 = 1 : 4 : 2 : 3 : 5]$, only yield monoximes.

F. S. K.

Dihydroxythiobenzenes. By G. TASSINARI (*Chem. Centr.*, 1888, 1354, from *Rend. Acad. dei Lincei* [4], 4, ii, 47—51).—The author considers that the compounds he has obtained, as well as their homologues, have a symmetrical constitution. Several isomeric compounds were never obtained at the same time. The reaction is much more violent when the compounds are prepared from phenols in which the para-position to the hydroxyl-group is free, and the derivatives so prepared have a higher melting point than their isomerides.

In the action of parabromophenol on sulphur dichloride, considerable quantities of each of the reacting substances remain unchanged. The *acetyl*-derivative of the dihydroxythiobenzene (Abstr., 1888, 805) melts at 86—87°. From this the *acetylhydroxysulphone* was prepared by oxidation; it forms colourless crystals, which are sparingly soluble in cold alcohol and insoluble in water; it softens at 160°, and melts at 186—187°. By dissolving it in a little alcoholic potash and re-acidifying, a hydroxysulphone, *hydroxysulphonebenzid*, $C_{12}H_{10}O_4S$, was obtained, which must be either a di-meta- or a di-ortho-derivative. It is white, crystalline, melts at 186—187°, and is soluble in alcohol, little soluble in water and in acetic acid. The acetylhydroxysulphone becomes readily soluble in potassic hydrate after heating to 187°; it is therefore probable that the acetyl-group becomes separated by heating.

In order to determine the constitution of the dihydroxythiobenzene melting at 150°, Annaheim's hydroxysulphonebenzide was nitrated, in order to obtain the di- and tetra-nitro-derivatives. Picric acid was formed, as is also the case when the nitro-derivatives of hydroxysulphonebenzid are boiled with nitric acid.

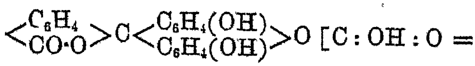
The *acetyl*-derivative of *orthodimethyldihydroxythiobenzene* crystallises from alcohol and melts at 44°. When oxidised with potassium permanganate, the corresponding *benzide*, $C_{14}H_{14}O_4S$, is formed, which melts at 132—133°, is insoluble in water, but soluble in hot alcohol. By saponifying with alcoholic potash, dimethylhydroxysulphonebenzide melting at 263° is formed; it dissolves in alkali hydroxides and carbonates, and is reprecipitated from these solutions by carbonic acid.

Diacetylparadimethyldihydroxythiobenzene melts at 83—84°, and when oxidised yields the corresponding *benzid* melting at 206—208°; the latter is little soluble in hot alcohol. Saponification with alcoholic potash gives *paradimethylhydroxysulphonebenzide*, which is rather soluble in alcohol and acetic acid, and melts at 209°; it dissolves in alkali hydroxides and carbonates, and is reprecipitated from such solutions by carbonic anhydride.

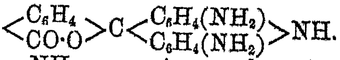
The *acetyl*-derivative of dihydroxythionaphthalene melts at 200°, is little soluble in, and decomposed by hot acetic acid. J. W. L.

Fluoresceïn. By R. MEYER and O. OPPELT (*Ber.*, **21**, 3376—3378).—When fluoresceïn is heated for eight hours with aqueous ammonia at 180—200°, a basic compound, $C_{20}H_{15}N_3O_2$, is formed, which on cooling crystallises in the tube in large, thick, reddish-yellow, monoclinic prisms and tables. It is a direct yellow dye for wool. The hydrochloride crystallises in tufts of reddish-yellow prisms, and from its very dilute and boiling solution, ammonia precipitates the base in scales of bronze-like lustre; under the microscope these are seen to consist of extremely characteristic X-like interpenetrating twins.

The authors point out that the constitution assigned to fluoresceïn by Knecht (*Annalen*, **215**, 83) is very improbable, and propose instead the formula



$$<\genfrac{}{}{0pt}{}{C_6H_4}{CO{\cdot}O}>C<\genfrac{}{}{0pt}{}{C_6H_4(OH)}{C_6H_4(OH)}>O \; [C:OH:O = 1:4:6],$$

that of the derived base being  $<\genfrac{}{}{0pt}{}{C_6H_4}{CO{\cdot}O}>C<\genfrac{}{}{0pt}{}{C_6H_4(NH_2)}{C_6H_4(NH_2)}>NH$. The base must contain at least one NH_2-group, inasmuch as its hydrochloride yields a diazo-compound when treated with nitrous acid. On treatment with cold aqueous soda, the lactone-ring is readily broken up, and the base yields a sodium salt crystallising in slender needles; the solution, when acidified and then precipitated by ammonia, is at once reconverted into the original base. Reduction with zinc-dust in the alkaline solution converts the sodium salt into a colourless compound, which is not precipitated on treatment first with hydrochloric acid and then with ammonia.

Orcinphthaleïn, when heated in like manner with aqueous ammonia, yields a base similar to that just described; the chief product, however, is a colourless, crystalline, neutral compound containing nitrogen. W. P. W.

Desmotropy in Phenols. By J. Herzig and S. Zeisel (*Monatsh.*, 9, 882—899).—An examination of the indifferent oil obtained in the preparation of pentethylphloroglucinol (Abstr., 1888, 822) has been undertaken. It was subjected to the action of hydrogen iodide, the product dissolved in ether, and then extracted with potash. The greater part is taken up by the potash, but a portion is not attacked and remains dissolved in the ether.

If the potash solution is acidified, and the product again dissolved in ether and crystallised, a crystalline mass is obtained, one portion of which is sparingly soluble in alcohol and melts at 209—212°, whilst the other is more readily soluble in alcohol, melts at 91—95°, and is in every way identical with the pentethylphloroglucinol already described. The sparingly soluble portion has the composition of a *tetrethylphloroglucinol.* One atom of the hydrogen is replaceable by a metal, and it is converted by the action of ethyl iodide into a monethyl salt, and by the action of acetic anhydride into a monacetate melting about 60—62°. It readily exchanges one atom of hydrogen for bromine, the product being probably a mixture of several isomerides. A similar reaction with bromine is found to occur in the case of pentethylphloroglucinol.

The portion of the original product, which is insoluble in potash, consists chiefly of a secondary hexethylphloroglucinol, which, as it is unattacked by hydrogen iodide, must be regarded as *hexethyltriketohexamethylene*, isomeric with the ethyl salt of the bi-secondary pentethylphloroglucinol already described. H. C.

Derivatives of Parabromobenzyl and Parachlorobenzyl Alcohols. By G. Errera (*Gazzetta*, 18, 236—243).—Parabromobenzyl chloride cannot be obtained by the bromination of benzyl chloride or by the action of chlorine on parabromotoluene, but the author has succeeded in preparing it from parabromobenzyl alcohol. The latter was prepared by Jackson and Lowery's method (Abstr., 1878, 64) of boiling parabromobenzyl bromide with water for several hours, using a reflux condenser, operating on small quantities at a time (4 to 5 grains) and using abundance of water (500 c.c.). The mixture bumps very much, but a metal vessel cannot be used as it acts on the bromide, in fact when the latter is boiled with zinc-dust nothing but paradibromobenzyl (m. p. 114°) is formed; the chloride is acted on in like manner.

The authors find that besides parabromobenzyl alcohol,

$$C_6H_4Br\cdot CH_2\cdot OH,$$

the corresponding ether is also formed; the two, however, can be easily separated by crystallisation from water, in which the latter is insoluble. The alcohol crystallises from water in long, flattened needles melting at 75°; Jackson and Lowery give 77°, the higher melting point being probably due to the presence of some of the ether.

Parabromobenzyl chloride, $C_6H_4Br\cdot CHCl_2$, is obtained when the alcohol is treated with phosphorus pentachloride, but as other products are formed at the same time, it is far better to heat the alcohol with fuming hydrochloric acid at 150° in closed tubes for three to four hours. The reaction is complete, and the chloride is obtained in a pure state by once recrystallising the product from alcohol. It forms lustrous, colourless needles which melt at 38—39°. It is very soluble in hot alcohol, and its vapour attacks the eyes, but much less than that of the bromide. It is isomorphous with parachlorobenzyl chloride and with parachlorobenzyl and parabromobenzyl bromides.

Parabromobenzyl ether, $(C_6H_4Br\cdot CH_2)_2O$.—As stated above, this ether is formed at the same time as the alcohol when parabromobenzyl bromide is boiled with water, and is left as an insoluble residue when the product is treated with boiling water. It may be purified by repeated crystallisation from boiling alcohol. It can also be prepared by the action of dehydrating agents, such as sulphuric acid, boric anhydride, or zinc chloride, on the alcohol; the two first-mentioned do not yield satisfactory results, but with zinc chloride the yield is almost theoretical. The ether crystallises from alcohol in long, flattened needles which melt at 85—86°. It is insoluble in water, and only sparingly soluble in alcohol even when boiling. If the ether is boiled for some time, it is decomposed, splitting up into parabromotoluene and parabromobenzaldehyde, $(C_6H_4Br\cdot CH_2)_2O = C_6H_4Br\cdot COH + C_6H_4Br\cdot CH_3$; these can be easily separated by distillation. The ether is attacked by nitric acid with formation of parabromobenzaldehyde and other products, but the amount of material at the author's disposal was too small to allow of a complete investigation of the reaction.

Parachlorobenzyl Ether, $(C_6H_4Cl\cdot CH_2)_2O$.—When parachlorobenzyl bromide is boiled with water or dilute soda solution, it does not behave like the bromine-derivative, as no trace of the ether is produced. The latter can be easily obtained, however, by boiling the alcohol with zinc chloride. It crystallises from alcohol in needles or plates which are much less soluble than parachlorobenzyl alcohol. It melts at 54—55°, and when boiled splits up into parachlorotoluene and parachlorobenzaldehyde. C. E. G.

Nitrobenzyl Ethyl Ethers. By G. ERRERA (*Gazzetta*, **18**, 232—235).—This is a continuation of former work (Abstr., 1887, 1103).

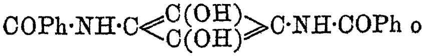
Paranitrobenzyl Ethyl Ether, $OEt\cdot CH_2\cdot C_6H_4\cdot NO_2$.—The general method for the preparation of the substituted benzyl ethyl ethers, that is, the action of alcoholic potash on the corresponding derivatives of benzyl chloride, is not applicable in the case of paranitrobenzyl ethyl ether, as paranitrobenzyl chloride under these circumstances is converted into paradinitrostilbene. In order to prepare it, the chloride is heated for a long time with ordinary alcohol in a close vessel in a boiling brine bath, as a higher temperature cannot be employed. The product, even after long heating, still contains much unaltered paranitrobenzyl chloride, and in order to remove it a few drops of alcoholic potash are added to the liquid whilst it is still hot; this at once converts the unattacked chloride into dinitrostilbene, which being almost insoluble in alcohol is precipitated, and can be removed by filtration. The potash is then neutralised with hydrochloric acid, and the product distilled with steam, when the ether passes over with the aqueous vapour, and solidifies on cooling. Paranitrobenzyl ethyl ether is pale yellow, and very soluble in alcohol and in ether, sparingly in light petroleum, from which it crystallises in needles, and insoluble in water. It melts at 24—24·5°, and at a higher temperature distils, but is at the same time partly decomposed. Treatment with fuming nitric acid converts it into paranitrobenzaldehyde.

Metanitrobenzyl Ethyl Ether.—This is prepared by heating metanitrobenzyl chloride with a slight excess of alcoholic potash on the water-bath, and, when the reaction is complete, neutralising the liquid with hydrochloric acid and distilling the product with a current of steam. This ether is a yellow oil, which solidifies to a crystalline mass in a mixture of snow and hydrochloric acid (melting point not given). It resembles the para-derivative in its behaviour to solvents, and yields metanitrobenzaldehyde when treated with nitric acid.

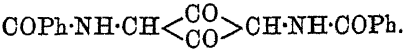
Orthonitrobenzyl Ethyl Ether.—The orthonitrobenzyl chloride employed for the preparation of this ether was obtained by the nitration of benzyl chloride. The liquid product, when cooled by a freezing mixture, deposits para- and ortho-nitrobenzyl chlorides which can be easily separated by fractional crystallisation. This may be much accelerated by introducing a crystal of one or other chloride into the supersaturated alcoholic solution, when crystals of the same species separate at once, while the other chloride remains in solution and is deposited later. It can then be obtained in a pure state by one recrystallisation. The orthonitrobenzyl ethyl ether, prepared like the para-derivative, is a yellow liquid which gradually becomes brown on exposure to the light. It does not solidify when cooled in a mixture of snow and hydrochloric acid, and is converted into orthonitrobenzaldehyde by the action of nitric acid. C. E. G.

Derivative of Tetrole and Synthesis of Tribenzamidophloroglucinol. By L. RÜGHEIMER (*Ber.*, 21, 3325—3331).—When ethyl hippurate (5 parts) is gradually heated with dry sodium ethoxide, so that in the course of about three hours the temperature rises to about 160—170°, alcohol distils, and on adding water to the residue two sodium salts are formed, one of which is only very sparingly soluble in dilute soda.

Dibenzamidodihydroxytetrole, $C_{18}H_{14}N_2O_4$, is obtained by separating the sparingly soluble sodium salt, dissolving it in boiling water, and adding hydrochloric acid to the warm filtered solution. It can also be prepared by heating ethyl hippurate with sodium at 160—170°. It crystallises from hot alcohol in needles containing $\frac{1}{2}$ mol. H_2O, loses its water at 108—110°, the anhydrous crystals melting at 137—138°. It is very readily soluble in hot benzene and alkalis, but only moderately so in alcohol; the alcoholic solution gives a violet coloration with ferric chloride. The *barium* salt is readily soluble in water. The *silver* salt is very unstable, and rapidly darkens. The *ethyl*-derivative was obtained in an impure state as an aromatic smelling oil; the acid seems to yield an acetyl-derivative when treated with acetic anhydride. When boiled for a long time with dilute hydrochloric acid, or better with eight times its weight of a mixture of equal parts of concentrated sulphuric acid, glacial acetic acid, and water, it is decomposed into benzoic acid and diamidoacetone. Its constitution is probably either



$\mathrm{COPh{\cdot}NH{\cdot}C}\Big<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{C(OH)}\end{matrix}\Big>\mathrm{C{\cdot}NH{\cdot}COPh}$ or



$$\mathrm{COPh{\cdot}NH{\cdot}CH}\Big<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\Big>\mathrm{CH{\cdot}NH{\cdot}COPh}.$$

Diamidoacetone platinochloride, $C_3H_8N_2O,H_2PtCl_6$, crystallises in small, orange plates, and turns bright yellow when warmed on the water-bath.

Tribenzamidophloroglucinol, $C_{27}H_{21}N_3O_6$, is formed when the readily soluble sodium salt obtained in the reaction described above is decomposed with hydrochloric acid. It crystallises from water in small needles containing 1½ mol. H_2O, and melting at 153·5—158·5°. It is very readily soluble in alcohol, but only very sparingly in hot water, and insoluble in ether; the alcoholic solution gives a blue coloration with a small quantity of ferric chloride, but on adding more of the reagent the colour changes to green. It is decomposed, with liberation of benzoic acid, when heated at a comparatively low temperature. The *lead* salt, $(C_{27}H_{18}N_3O_6)_2Pb_3$, is sparingly soluble in water, but the *calcium*, *barium*, and *silver* salts are readily soluble. The *copper* salt, $(C_{27}H_{18}N_3O_6)_2Cu_6$, is bright green. F. S. K.

Azotoluenes. By J. V. Janovsky (*Monatsh.*, 9, 828—841).—*Parazotoluene* is best prepared by adding to 100 parts of 20 per cent. aqueous soda heated to 100°, 100 parts of paranitrotoluene, and then adding slowly and with constant agitation 100—110 parts of zinc-dust. An orange-coloured oil is formed, which should at once be separated from the solution, and left to crystallise. One recrystallisation from glacial acetic acid is sufficient to obtain pure parazotoluene melting at 144°. It crystallises in rhombic needles, soluble in alcohol, ether, benzene, and light petroleum, and also in boiling hydrochloric acid. When oxidised with chromic mixture it gives an orange-coloured crystalline compound melting at 132°.

The acetic acid mother-liquor from the parazotoluene contains three other products which melt at 109°, 75°, and 70° respectively. The last of these is identical with the β-azoxytoluene of Melms and Petrieff, whilst the compound melting at 75° appears to be a peculiar isomeride of the same. Both these compounds yield two bromides when treated with bromine (2 mols.), those from the first melting at 85° and 57°, those from the second at 92° and 57°.

By acting with nitric acid on the bromide of parazotoluene melting at 128° (Abstr., 1888, 686), a nitrobromo-derivative melting at 138° has been obtained.

The nitration of parazotoluene with nitric acid of sp. gr. 1·5 yields chiefly *trinitro*-derivatives. Two of these are formed, one (α) melting at 189°, and the other (β) at 138°. A dinitro-compound melting at 114° is obtained at the same time. All these compounds give sulphonic acids with fuming sulphuric acid. By the further treatment of α-trinitrazotoluene with nitric acid, a *tetranitrazotoluene* melting at 198—200° is produced, and β-trinitrazotoluene when nitrated gives the same compound. A mononitrazotoluene is formed on treating parazotoluene with nitric acid of sp. gr. 1·45. It melts at 80°, and on further nitration yields the dinitro-compound melting at 114°. H. C.

Halogen-derivatives of Phenylhydrazine. By A. NEUFELD (*Annalen*, **248**, 93—99).—The preparation of parachloro- and parabromo-phenylhydrazine from the corresponding aniline-derivatives has already been described by Elsinghorst (*Inaug. Diss.*, *Erlangen*, 1884). These substances readily unite with aldehydes and ketones. *Acetoneparabromophenylhydrazone* crystallises in glistening plates and melts at 93°. *Acetaldehydeparabromophenylhydrazone* forms yellow needles and melts at 83°.

Dibromophenylhydrazine, $[N_2H_3 : Br_2 = 1 : 2 : 5]$, prepared from dibromaniline by reduction with stannous chloride or sodium sulphite, melts at 97°, and is freely soluble in alcohol, ether, and benzene. The hydrochloride is crystalline. *Symmetrical tribromophenylhydrazine*, $[N_2H_3 : Br_3 = 1 : 2 : 4 : 6]$, melts with decomposition at 146°. It is soluble in benzene, chloroform, warm alcohol and hot water. The hydrochloride and sulphate are stable salts. The acetone compound melts at 54.° *Tetrabromophenylhydrazine*,

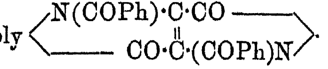
$$[N_2N_3 : Br_4 = 1 : 2 : 3 : 4 : 6],$$

crystallises in prisms and melts at 167°. It dissolves in chloroform, benzene, and hot water. The hydrochloride is crystalline. The compounds with acetone and acetaldehyde are solid.

Pariodophenylhydrazine melts at 103°, and is freely soluble in alcohol, ether, chloroform, benzene, and acetic acid. The acetone compound crystallises in plates and melts at 114°. *Metadi-idophenylhydrazine*, $[N_2H_3 : I_2 = 1 : 2 : 4]$, forms silky crystals, which melt at 112° and are freely soluble in alcohol, ether, and benzene. The hydrochloride melts at 163° with decomposition. The base unites with acetone and acetaldehyde to form hydrazones. W. C. W.

Phenylhydrazones. By O. RUDOLPH (*Annalen*, **248**, 99—105).—*Metatoluylaldehydephenylhydrazone* is deposited when a solution of phenylhydrazine in acetic acid is added to toluylaldehyde suspended in water. The compound crystallises in prisms, melts at 87—88·5°, and dissolves in ether, chloroform, and alcohol. *Cumaldehydephenylhydrazone* melts at 127—129°. It rapidly turns red on exposure to the light. *Diphenylacetaldehydephenylhydrazone* is freely soluble in hot alcohol. *Metahydroxybenzaldehydephenylhydrazone*, prepared from metamidobenzaldehyde, forms colourless prisms. It melts at 130—131·5°, and dissolves freely in warm alcohol, chloroform, benzene, or acetic acid. *Parahydroxybenzaldehydephenylhydrazone* melts at 177—178° and is freely soluble in ether. *Anisaldehydephenylhydrazone* forms white needles or plates and melts at 120—121°. It is freely soluble in ether and in hot alcohol or benzene. *Piperonalphenylhydrazone* melts at 102—103°. *β-Resorcylaldehydephenylhydrazone* melts with decomposition between 156° and 160°. It dissolves freely in the usual solvents. *Resorcindialdehydephenylhydrazone* melts about 230° with decomposition. It dissolves in warm solutions of the alkalis. W. C. W.

Phenyltrimethylenimine. By L. BALBIANO (*Chem. Centr.*, 1888, 1356, from *Rend. Acad. dei Lincei* [4], **4**, ii, 44—46).—If dry phenyltrimethylenediamine hydrochloride is heated over a bare flame until the whole of the salt has volatilised, and the vapours are condensed in dilute hydrochloric acid, *phenyltrimethylenimine* and ammonium chloride are found in the solution. From the solution of the distillate, after concentrating to a syrup, alcohol precipitates the latter, whilst the base is separated from the solution by acidifying with hydrochloric acid, precipitating with potassium bismuth iodide, and washing the red precipitate. After treating with potash and distilling with steam, it may be precipitated as the platinochloride $C_3H_6\colon NPh,H_2PtCl_6$, an orange, crystalline compound, soluble in hot water. The hydrochloride could not be obtained in crystals from the aqueous solution. J. W. L.

Hippuroflavin. By L. RÜGHEIMER (*Ber.*, **21**, 3321—3325)—*Hippuroflavin*, $C_9H_5NO_2$, is prepared by gradually heating a mixture of ethyl hippurate (1 mol.) and phosphorus pentachloride (1 mol.) until the latter is dissolved, and then adding a little more phosphorus pentachloride and heating at 160° for about eight hours. The whole is poured into alcohol, and the crystalline product collected and washed with alcohol. It separates from hot nitrobenzene or hot glacial acetic acid in small, yellow crystals, partially decomposes, but without melting, when heated at 300°, and sublimes with partial decomposition in citron-yellow crystals. It is very sparingly soluble in glacial acetic acid and nitrobenzene, and almost insoluble in water, alcohol, and ether. When warmed with alcoholic soda, it is decomposed with evolution of ammonia, and when heated at 100° for 8 to 9 hours with concentrated ammonia the red solution obtained deposits a colourless, crystalline compound. It yields benzoic acid when warmed with alkaline potassium permanganate, or when heated at 130° with nitric acid of sp. gr. 1·15; and when treated with concentrated hydrochloric acid at 110°, it is completely decomposed into benzene, carbon, and dark-coloured products. When boiled with zinc-dust and glacial acetic acid, it yields a yellowish substance which dissolves in soda with a brown coloration, but is reprecipitated in greenish flocks on adding hydrochloric acid. It is gradually converted into a colourless compound when warmed with stannous chloride and hydrochloric acid in glacial acetic acid solution. Its constitution is probably  $\left\langle\begin{matrix}N(COPh)\cdot C\cdot CO\text{———}\\ \|\\ \text{———}CO\cdot C\cdot(COPh)N\end{matrix}\right\rangle$. F. S. K.

Phthalimidine and Methylphthalimidine. By P. Barbier (*Compt. rend.*, **107**, 918—921).—Phthalimidine is readily obtained by the gradual addition of small quantities of hydrochloric acid to an acetic acid solution of phthalimide containing the calculated quantity of granulated tin. It forms white needles melting at 150°, and can be recrystallised from boiling water; it is isomeric with oxindole, and is both an amine and an amide. It forms an unstable hydrochloride which can only exist in presence of free acid, and loses all its hydrochloric acid in a vacuum. The hydrochloride is completely decomposed by water; the platinochloride, $(C_8H_7NO)_2,H_2PtCl_6$, and the aurochloride, $(C_8H_7NO,HCl)_3,2AuCl_3$, are both unstable. A derivative, C_8H_6NOAg, is obtained as a white precipitate by adding silver nitrate to a solution of phthalimidine in potassium hydroxide solution.

When a solution of phthalimidine in potassium hydroxide is heated in sealed tubes at 100° for six hours with excess of methyl iodide, methylphthalimidine, C_9H_9NO, is obtained in slender, white needles, which melt at 120°. It forms an unstable hydrochloride and an unstable aurochloride, $(C_9H_9NO)_2,HAuCl_4$. The properties of methyl phthalimidine indicate that it has the constitution $C_6H_4<\substack{CO\\CH_2}>NMe$, and not $C_6H_4<\substack{CH_2\cdot NH\\CO\cdot CH_2}>$. This view is confirmed by the fact that a concentrated alcoholic solution of methylamine yields methylphthalimidine when heated with phthalide at 220° for 12 hours.

C. H. B.

Derivatives of Diphenylacetaldehyde. By W. G. M. Weise (*Annalen*, **248**, 34—56). Hydrobenzoïn is most conveniently prepared from benzoïn by the method described by Breuer and Zincke (Abstr., 1880, 118). It is converted into diphenylacetaldehyde by treatment with dilute sulphuric acid at 200°; this substance is converted into a nitrile by adding powdered potassium cyanide, and finally hydrochloric acid to its ethereal solution. When dry hydrogen chloride is passed into a mixture of the nitrile and absolute alcohol (in molecular proportions), crystals of *ethyl β-diphenylimidolactate hydrochloride*, $CHPh_2\cdot CH(OH)C(OEt){:}NH,HCl$, are deposited. The hydrochloride melts at 135° with decomposition; it is also decomposed by dissolution in water, yielding in this case ammonium chloride and *ethyl β-diphenyllactate*. The latter is a micro-crystalline powder, melts at 66°, and yields a monacetyl-derivative, $CHPh_2\cdot CH(OAc)\cdot COOEt$, melting at 53°. *β-Diphenyllactic acid*, $CHPh_2\cdot CH(OH)\cdot COOH$, crystallises in needles, and melts at 159°. It is freely soluble in alcohol, ether, and hot water. The salts of this acid do not readily crystallise. At 170° the acid is converted into the *anhydride*, $COOH\cdot CH(CHPh_2)\cdot O\cdot CO\cdot CH(OH)\cdot CHPh_2$. Hydriodic acid decomposes β-diphenyllactic acid at 150° into carbonic anhydride and

diphenylethane. If the reaction takes place at a higher temperature, dibenzyl is also formed.
W. C. W.

Passivity of certain Polyketones towards Hydroxylamine and Phenylhydrazine. By J. HERZIG and S. ZEISEL (*Ber.*, 21, 3493—3494; compare Kehrmann, this vol., p. 243).—Tetrethyl- and pentethyl-phloroglucinol (Abstr., 1888, 822) do not react with hydroxylamine or phenylhydrazine, and it would therefore seem that meta-diketones no longer give the characteristic ketonic reaction with these compounds when the hydrogen-atoms in the ortho-positions to the carbonyl-groups are almost completely or completely replaced by alkyl-groups.
W. P. W.

Nitriles. By J. A. MILLER (*Chem. Centr.*, 1888, 1359).—Paramethoxybenzaldehyde reacts with hydroxylamine with formation of *paramethoxybenzaldoxime*, $\mathrm{OMe\cdot C_6H_4\cdot CH{:}NOH}$, melting at 64°. By the action of sodium nitrite and hydrochloric acid, the aldehyde is regenerated. When heated with acetic chloride, the *nitrile*, $\mathrm{OMe\cdot C_6H_4\cdot CN}$, is formed, which melts at 61—62°. By treating this nitrile with hydroxylamine hydrochloride and soda, *paramethoxybenzenylamidoxime*, $\mathrm{OMe\cdot C_6H_4\cdot C(NH_2){:}NOH}$, is formed, melting at 122—123°. Its hydrochloride melts at 168°. *Paramethoxybenzenylamidoxime ethyl ether*, $\mathrm{OMe\cdot C_6H_4\cdot C(NH_2){:}NOEt}$, melting at 51—52°, is prepared by heating the amidoxime with sodium ethoxide and ethyl iodide.

Paramethoxylbenzenylacetylamidoxime, $\mathrm{OMe\cdot C_6H_4\cdot C(NH_2){:}NOAc}$, is formed when a chloroform solution of the amidoxime is treated with acetic chloride.

Paramethoxybenzenylethenylazoxime, $\mathrm{OMe\cdot C_6H_4\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{N\cdot O}}{>}\mathrm{CMe}$, melting at 68°, is formed by heating the acetyl compound, or by the direct action of acetic anhydride on the amidoxime. With acetaldehyde, *paramethoxybenzenylethylideneimidoxime*,

$$\mathrm{OMe\cdot C_6H_4\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N\cdot O}}{>}\mathrm{CHMe},$$

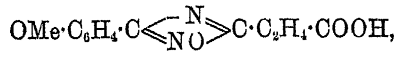
melting at 127·5° is formed. The *ethyl carbonate* of the amidoxime, $\mathrm{OMe\cdot C_6H_4\cdot C(NH_2){:}N\cdot O\cdot COOEt}$, melting at 119—120°, is formed by the action of ethyl chlorocarbonate on the amidoxime in chloroform solution. When treated with solution of soda or potash, this carbonate is changed into *paramethoxybenzenylimidoximecarbonyl*; this may also be prepared by heating the chlorocarbonate with the amidoxime. It melts at 208°.

Paramethoxybenzoylbenzenylamidoxime, $\mathrm{OMe\cdot C_6H_4\cdot C(NH_2){:}N\cdot OBz}$, melting at 148°, is prepared by the action of the amidoxime in alkaline solution on benzoic chloride at the ordinary temperature. If heat be employed *paramethoxybenzenylazoximebenzenyl*,

$$\mathrm{OMe\cdot C_6H_4\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{N\cdot O}}{\mathrm{N}}{>}\mathrm{CPh},$$

is formed, which melts at 102°.

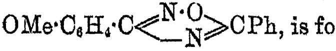
Paramethoxybenzenylazoximepropenyl-ω-carboxylic acid,



$$OMe{\cdot}C_6H_4{\cdot}C\begin{matrix}\diagup N \diagdown \\ \diagdown NO \diagup\end{matrix}C{\cdot}C_2H_4{\cdot}COOH,$$

melting at 140—141°, is formed by melting succinic anhydride with the amidoxime.

The salicyl derivatives are formed in a similar manner.

Salicylaldoxime melts at 57°; *salicylonitrile*, $OH{\cdot}C_6H_4{\cdot}CN$, melts at 99—100°; a polynitrile is formed at the same time as a secondary product; it is decomposed on heating with concentrated hydrochloric acid at 200° into phenol, carbonic anhydride, and ammonia. *Salicylamidoxime*, $OH{\cdot}C_6H_4{\cdot}C(NH_2){:}NOH$, melts at 98·5°. *Salicylamidoxime ethyl carbonate*, $OH{\cdot}C_6H_4{\cdot}C(NH_2){:}N{\cdot}O{\cdot}COOEt$, melts at 96°. *Salicylamidoximepropenyl-ω-carboxylic acid* melts at 116—117°. *Orthomethoxybenzonitrile*, $OMe{\cdot}C_6H_4{\cdot}CN$, boiling point 255—256°, is prepared from salicylonitrile by the action of methyl iodide; *orthomethoxybenzenylamidoxime*, $OMe{\cdot}C_6H_4{\cdot}C(NH_2){:}NOH$, melting at 123°, is formed from the last-named substance by the action of hydroxylamine. By melting this amidoxime with benzoic chloride, *orthomethoxybenzenylazoximebenzenyl*,  $OMe{\cdot}C_6H_4{\cdot}C\begin{matrix}\diagup N{\cdot}O \diagdown \\ \diagdown N \diagup\end{matrix}CPh$, is formed; it melts at 117°. J. W. L.

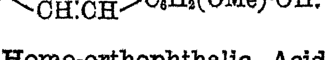
Derivatives of Metamethylphenylacetic Acid. By M. SÉNKOWSKI (*Monatsh.*, 9, 854—856).—*Methyl metamethylphenylacetate* is prepared by saturating a solution of the acid in five times the amount of methyl alcohol with hydrochloric acid. It is a liquid of sp. gr. 1·044 at 17·5°, boiling at 228—229°. The *ethyl* salt, prepared in similar manner, has a sp. gr. of 1·018 at 17·5°, and boils at 237—238°.

By dissolving metamethylphenylacetic acid in concentrated nitric acid, carefully cooled, a product is formed which melts at 70—110°, but cannot be obtained of constant melting point. It gives an ethyl salt which is still liquid at −30°. If the nitric acid solution of the acid is heated for some minutes on the water-bath, a *dinitro*-derivative, $C_6H_2Me(NO_2)_2{\cdot}CH_2{\cdot}COOH$, is obtained, melting at 173—174°. The salts of this acid are very unstable, decomposing in aqueous solution even at the ordinary temperature into dinitro-xylene and carbonic anhydride. The *methyl* salt, prepared by saturating the solution of the acid in methyl alcohol with hydrogen chloride, crystallises in yellow needles melting at 41°. The *ethyl* salt, similarly prepared, melts at 68°. H. C.

Scopoletin. By D. TAKAHASHI (*Chem. Centr.*, 1888, 1364—1365, from *Mitt. med. Fak. Univ. Tokio*).—Scopoletin, $C_{10}H_8O_4$, the fluorescent substance occurring in *Scopolia japonica*, is extracted from the roots by treatment with alcohol, evaporation of the alcoholic solution, treatment with strong hydrochloric acid, drying with admixture of sand, extraction with chloroform, and finally recrystallisation several times from absolute alcohol. It consists of colourless needles, melting at 198—199°, little soluble in cold water, readily soluble in alcohol, ether, and chloroform. *Acetylscopoletin*, $C_{10}H_7O_4Ac$, melts at 176°, and is little soluble in water, but soluble in alcohol. *Benzoylscopoletin* is insoluble in water, little soluble in alcohol, and melts at 158°. *Methylscopoletin*, $C_{10}H_7O_4Me$, is prepared by heating a mixture of scopoletin (1 mol.), methyl iodide (2 mols.), and potassium hydroxide (2 mols.), in methyl alcohol on the water-bath. It forms long, colourless needles, melts at 144°, is insoluble in cold water, soluble in hot water, alcohol, ether, benzene, and carbon bisulphide, insoluble in alkalis in the cold. This characteristic, together with the partial decrease in the fluorescence in alkaline solution indicate, in the same way as the characteristic reactions of coumarin, that scopoletin is also a coumarin-derivative.

Since dimethylæsculetin and methylscopoletin have been proved to be identical, and since also the bromine-derivatives are alike, scopoletin must be a derivative of hydroxyquinol. *Methylscopoletilic acid*, $C_{11}H_{10}O_5$, is prepared by heating monobromomethylscopoletin with potash, a reaction which is also similar to those which the dibromo-derivatives of coumarin undergo when heated with potash. If its silver salt is decomposed by carbonic anhydride, a colourless, pleasant-smelling oil is obtained, which, when treated with strong aqueous soda and distilled with steam, becomes converted into dimethoxycoumarin, $C_{10}H_{10}O_3$, melting at 58°.

Methyl trimethylæsculetate, $C_6H_2(MeO)_3\cdot CH{:}CH\cdot COOMe$, is prepared by melting methylscopoletin with potash, extracting the mass with methyl alcohol, and heating with methyl iodide in a closed flask for three hours. By recrystallising several times from alcohol the product remaining after the alcohol has been evaporated off, it is obtained as a yellow, crystalline substance, melting at 102°, insoluble in water, but readily soluble in alcohol and ether; it yields the free acid on hydrolysis, &c. By reduction with sodium amalgam, *trimethoxyphenylpropionic acid*, $C_6H_2(OMe)_3\cdot CH_2\cdot CH_2\cdot COOH$, is formed, from which by oxidation with potassium permanganate trimethoxybenzoic acid is obtained. From this, trimethoxyquinol can be obtained; the constitution of scopoletin is, therefore, concluded to be



$<\begin{matrix}CO—O\\CH{:}CH\end{matrix}>C_6H_2(OMe)\cdot OH$.

J. W. L.

Homo-orthophthalic Acid. By M. LE BLANC (*Chem. Centr.*, 1888, 1352—1353).

—*Dipropylhomo-orthophthalimide*, $C_9H_5Pr_2NO_2$, prepared by the action of propyl iodide on homo-orthophthalimide in alcoholic solution, melts at 141·5°. *Dipropylhomo-orthophthalic anhydride*, $C_9H_4Pr_2O_3$, prepared by heating the imide at 240° with fuming hydrochloric acid, melts at 88°. *Dipropylhomo-orthophthalic acid*, $C_9H_6Pr_2O_4$, prepared by treating the anhydride with potash, melts at 127°. *Homo-orthophthalopropylimide*, prepared by distilling a solution of homo-orthophthalic acid in propylamine, crystallises in leaves which melt at 69—70°. *Nitrobenzenehomo-orthophthalopropylimide*, prepared from the last-named imide by treating it with nitrobenzaldehyde, melts at 119°. *Salicylhomo-orthophthalopropylimide*, prepared in like manner to the last-named compound, melts at 157°. Aldehydes of the fatty series, such as isovaleraldehyde, react in a manner quite different from the aromatic aldehydes.

Dibromo-orthophthalimide, prepared by the action of bromine on phthalimide in acetic acid solution, melts at 168·5°. J. W. L.

Synthesis of Dialkyl Phthalides. By R. Kothe (*Annalen*, **248**, 56—71).—*Dimethylphthalide*, $C_6H_4<\begin{matrix}CMe_2\\CO\end{matrix}>O$, prepared by acting on a mixture of methyl iodide and phthalic anhydride with zinc-dust, melts at 67—68°, and boils at 270—271°. It is easily obtained in large crystals, exhibiting the phenomenon of double refraction. It dissolves in a solution of potassium hydroxide, forming the potassium salt of orthohydroxyisopropylbenzoic acid. Reduction with sodium amalgam converts dimethylphthalide into dimethylhydrophthalide, $C_6H_4<\begin{matrix}CMe_2\\CH(OH)\end{matrix}>O$, and hydriodic acid reduces it to orthoisopropylbenzoic acid. Potassium cyanide acts on dimethylphthalide at 250°; dilute sulphuric acid converts the product into an acid, probably orthopropenylbenzoic acid. The acid melts at 60—61°, and forms a crystalline barium and silver salt.

Diethylphthalide is an oily liquid boiling at 210—214° under 210 mm. pressure. It appears to be identical with the compound described by Wischin (*Annalen*, **143**, 262).

Benzyl chloride acts energetically on a mixture of zinc-dust and phthalic anhydride, yielding an amorphous product soluble in ether and benzene. This substance melts at 73°, and is non-volatile. It does not contain oxygen. W. C. W.

γ-Ketonic Acids. By A. Dittrich and C. Paal (*Ber.*, **21**, 3451—3457).—*Ethyl β-benzoyl-α-ethylisosuccinate* (*ethyl phenacylethylmalonate*), $COPh·CH_2·CEt(COOEt)_2$, is prepared by treating ethylic ethylsodomalonate suspended in absolute ether with the calculated quantity of bromacetophenone (phenacyl bromide). It is an oil which dissolves in the ordinary organic solvents, and decomposes when distilled in a vacuum. The corresponding *acid* crystallises from most solvents in slender, white needles or long scales, but can be obtained in cruciform aggregates of fairly large, four-sided prisms with oblique terminal faces, by the slow evaporation of its solution in a mixture of chloroform and light petroleum; the prisms, however, contain chloroform of crystallisation and effloresce on exposure to the air. The acid melts at 150° with evolution of carbonic anhydride; is insoluble in light petroleum, sparingly soluble in hot water and benzene, and readily soluble in alcohol, ether, chloroform, and acetic acid. Treatment with phosphorus pentachloride converts it into the *dichloride*, which is readily decomposed by water. The *ammonium*, *potassium*, *calcium* (1 mol. H_2O), and *silver* salts are described. The *hydrazone*, $C_{25}H_{26}N_4O_3$, crystallises in concentrically-grouped, slender, white needles, melts at 132°, is readily soluble in the ordinary organic solvents, and, when heated above its melting point, loses carbonic anhydride and is converted into a substance insoluble in alkalis or alkaline carbonates.

β-Benzoyl-α-ethylpropionic acid (*phenacylethylacetic acid*), $COPh·CH_2·CHEt·COOH$, is formed when β-benzoyl-α-ethylisosuccinic acid is heated above its melting point. It crystallises from acetic acid in small aggregates, melts at 81—83°, decomposes on distillation, and yields a *hydrazone* insoluble in alkalis. The *calcium* salt, $(C_{12}H_{13}O_3)_2Ca + H_2O$, crystallises in white scales and is insoluble in absolute alcohol, but readily soluble in water; the *ethyl* salt is a yellowish oil.

2 : 4-*Phenylethylthiophen*, C_4H_2SPhEt, is obtained by distilling sodium β-benzoyl-α-ethylpropionate or sodium hydrogenβ-benzoyl-α-ethylisosuccinate with phosphorus pentasulphide. It crystallises in small, white scales, melts at about 40°, and has the characteristic odour of the two known phenylethylthiophens. W. P. W.

Reissert's Deoxypyranilpyroic Dibromide and Bromodeoxypyranilpyroic Acid. By R. ANSCHÜTZ and F. HENSEL (*Annalen*, **248**, 269—281).—The authors have previously shown (Abstr., 1888, 1092) that Reissert's dihydropyranilpyroic acid (Abstr., 1888, 696) is identical with the pyrotartaric-anilic acid. On repeating Reissert's experiments on the action of bromine-water on dihydropyranilpyroic acid, they find that the so-called deoxypyranilpyroic dibromide consists of a mixture of tribromaniline and pyrotartaric-parabromanilic acid, and the so-called monobromodeoxypyranilpyroic acid is impure pyrotartaric-parabromanilic acid.

Pyrotartaric-parabromanilic acid is the chief product of the reaction of bromine-water on sodium pyrotartrate; no tribromaniline is produced.

Parabromaniline unites with pyrotartaric anhydride in benzene solution, forming the parabromanilic acid of pyrotartaric acid (m. p. 158—158·5°). It is converted into the corresponding parabromanil by the action of phosphorus pentachloride.

Dibromaniline [1 : 2 : 4] yields a pyrotartaric-dibromanilic acid melting at 139°; but tribromaniline does not combine with pyrotartaric anhydride in solution in benzene. W. C. W.

Dyes from Diamidoethoxydiphenylsulphonic Acid. By A. FEER and H. MÜLLER (*Chem. Centr.*, 1888, 1358, from *Bull. Soc. indust. Mulhouse*, 1888, 488—490).—Diazobenzene and sodium paraphenolsulphonate react together with formation of a dye, of the constitution $PhN_2\cdot C_6H_3(OH)\cdot SO_3Na$ [= 1 : 4], of light-yellow colour, little soluble in cold water, readily so in alkaline solutions. If this is heated in a sealed tube with ethyl bromide and soda in molecular proportion, the corresponding ethyl salt of *ethoxyazobenzenesulphonic acid* is formed. Reduction with stannous chloride in hydrochloric acid or with zinc-dust in alkaline alcoholic solution leads to the formation of *diamidoethoxydiphenylsulphonic acid*,

$$NH_2\cdot C_6H_4\cdot C_6H_4(NH_2)(OEt)\cdot SO_3H\ [OEt : SO_3H = 1 : 4].$$

Sodium acetate precipitates the free acid in crystals from its concentrated solution. By treating the hydrochloric acid solution of this sulphonic acid with sodium nitrite (2 mols.), tetrazoethoxydiphenylsulphonic acid is obtained, which, by treatment with phenol (2 mols.) or amines in dilute alkaline solution, yields yellow, red, and violet dyes;

these dye cotton without the use of a mordant, although the dye is not so fast as when one is used. J. W. L.

Indole-derivatives. By L. Wolff (*Ber.*, **21**, 3360—3366).—3 : 2′ : 3′-*Trimethylindole*, $C_{11}H_{13}N$, is obtained when β-bromolevulinic acid is heated with three times its weight of paratoluidine. It crystallises in white scales having a peculiar odour, melts at 121·5°, boils at 297° (corr.), is volatile with steam, and dissolves sparingly in water, but readily in alcohol, chloroform, and light petroleum. When allowed to remain for a few days, it becomes yellow and finally brown, and its acetic acid solution is coloured at first green and afterwards an intense blue on boiling with a small quantity of ferric chloride. The *picrate* crystallises from alcohol in brownish-red needles, and melts at 189°; the *nitroso*-derivative, $C_{11}H_{12}N{\cdot}NO$, forms lustrous, golden-yellow needles, melts at 73°, and is sparingly soluble in water, readily soluble in alcohol and acetic acid.

1 : 2′ : 3′-*Trimethylindole*, prepared in like manner from orthotoluidine, crystallises in white scales, melts at 79°, boils at 282—283°, and closely resembles the 3 : 2′ : 3′-derivative in its solubility and behaviour with ferric chloride. The *picrate*, $C_{11}H_{13}N,C_6H_2(NO_2)_3{\cdot}OH$, crystallises in purple-red needles, and melts at 152°.

Ethyldimethylindole, [Et : Me : Me = 1′ : 2′ : 3′], obtained in like manner from ethylaniline, is a yellow oil which boils at 280—282°, has the persistent indole odour, dissolves readily in alcohol, ether, and benzene, and when boiled in acetic acid solution with a small quantity of ferric chloride or potassium dichromate, yields a very characteristic, intense red coloration. The *picrate*, $C_{12}H_{15}N,C_6H_2(NO_2)_3{\cdot}OH$, crystallises in small, dark-red needles, melts at 105°, and is soluble in benzene.

2″ : 3″-*Dimethyl-β-naphthindole*, formed under similar conditions from β-naphthylamine, crystallises from alcohol in colourless, brittle, strongly refractive tablets, melts at 132°, boils above 360°, and is only slightly volatile with steam. It is insoluble in water, soluble in alcohol and acetic acid, and readily soluble in ether and benzene, and its solution in acetic acid is coloured green on boiling with ferric chloride. The *picrate* crystallises in lustrous, dark-brown needles melting at 175°.

2″ : 3″-*Dimethyl-α-naphthindole*, prepared in like manner from α-naphthylamine, crystallises from alcohol in small, white granules or prisms, melts at 150°, and is insoluble in water, sparingly soluble in cold alcohol and acetic acid, and readily soluble in ether and benzene. When heated in acetic acid solution with a trace of ferric chloride, it yields a beautiful cherry-red coloration, whilst with potassium dichromate it gives an intense blue. W. P. W.

Indoles. By B. Trenkler (*Annalen*, **248**, 106—113).—Valeraldehydephenylhydrazone boils at 220° under a pressure of 150 mm. It is converted into 3′-isopropylindole by fusion with zinc chloride. 3′-*Isopropylindole* is a pale-yellow, crystalline mass freely soluble in alcohol, ether, benzene, chloroform, light petroleum, and acetic acid. It boils at 287—288°. The picrate crystallises in needles and melts at 98—99°. *Hydroisopropylindole*, prepared by the action of zinc-dust and strong hydrochloric acid on an alcoholic solution of isopropylindole, resembles hydroscatole in its properties (Abstr., 1887, 957).

3′-*Pentylindole*, from œnanthaldehydephenylhydrazone, boils at 345—347° and is freely soluble in alcohol, ether, and benzene. The picrate is crystalline. 2′ : 3′-*Methylphenylindole*, from methylbenzylketonephenylhydrazone, crystallises in colourless prisms and melts at 59—60°. It does not stain pinewood. The picrate and the nitroso-compound are crystalline. 2′ : 3′-*Benzylphenylindole*, from dibenzylketone, forms six-sided prisms and melts at 100—101°. It is freely soluble in alcohol, ether, benzene, chloroform, and acetic acid, and does not exhibit the pinewood reaction. W. C. W.

Decomposition of Benzidine Hydrochlorides by Water. By P PETIT (*Compt. rend.*, **107**, 839—841).—Benzidine monohydrochloride is stable in solution, and when potassium sulphate is added, an insoluble sulphate, $(C_{12}H_{12}N_2)_2,H_2SO_4$, is precipitated, but no free acid is liberated. In the case of the dihydrochloride, dissociation takes place according to two distinct laws. If the concentration of the solution does not exceed 5·4 grams per litre, a constant fraction (0·034) of the salt is dissociated into the monohydrochloride and hydrochloric acid. When the concentration exceeds 5·4 grams, part of the monohydrochloride formed is precipitated and the quantity of dihydrochloride decomposed is the sum of two quantities, namely, the fraction corresponding with a concentration of 5·4 grams, and a quantity proportional to the excess of dihydrochloride over and above 5·4 grams per litre. C. H. B.

Similar Reactions of Carbazole and Pyrroline. By S. C. HOOKER (*Ber.*, **21**, 3299—3301).—Carbazole, like pyrroline, gives the pinewood reaction, a fact which is not in accordance with Fischer's conclusion respecting this reaction (compare Abstr., 1886, 806). Carbazole gives with isatin and concentrated sulphuric acid a deep blue solution, from which water precipitates an indigo-blue substance, the colour of which rapidly becomes lighter. When a small quantity of sulphuric acid, diluted with one or two volumes of acetic acid, is added to an acetic acid solution of carbazole and quinone, a carmine-red solution is obtained, from which water precipitates a red or reddish-violet substance, soluble in ether, chloroform, and alcohol. (Compare Meyer and Stadler, Abstr., 1884, 1045.) A green solution is produced when oxidising agents, such as quinone, are added to a solution of carbazole in sulphuric acid, and the colouring matter, which is precipitated by water, is insoluble in ether. (Compare Gräbe and Glaser, this Journal, 1872, 302.) Pyrroline also yields a green substance when treated with a very small quantity of an oxidising agent in dilute sulphuric acid solution; this green compound is rapidly destroyed by strong oxidising agents. (Compare Meyer and Stadler, *loc. cit.*).

Pyrroline yields a crystalline compound with picric acid; it melts at about 71° and is unstable. Phenylpyrroline also combines with picric acid. F. S. K.

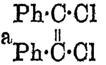
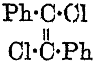
Malachite-green and Derivatives of Paramidodiphenylmethane. By A. MANNS (*Chem. Centr.*, 1888, 1363).—The leuco-base of malachite-green, when distilled over zinc-dust, is reduced to aniline, dimethylaniline, and paramidodiphenylmethane, together with hydrocarbons of the fatty and aromatic series.

Paramidodiphenylmethane was prepared synthetically from paranitrobenzyl chloride by means of Friedel-Craft's aluminium chloride reaction in benzene solution.

Nitrodiphenylmethane thus obtained melts at 30—31°. It is reduced by tin and hydrochloric acid to *paramidodiphenylmethane*, and from this *diazoamidodiphenylmethane*, $C_{26}H_{23}N_3$, is prepared by treatment with nitrous acid. *Methylparamidodiphenylmethane*, $C_{13}H_{11}\cdot NHMe$, is obtained from amidodiphenylmethane by the action of methyl iodide; it boils above 360°, and is a light yellow oil. The hydriodide melts at 150°. *Acetylparamidodiphenylmethane* melts at 127·5°; the *benzoyl*-derivative melts at 162°. *Diphenylmethane hydrazine*, $C_{13}H_{11}\cdot NH\cdot NH_2$, is obtained as hydrochloride by reducing diazodiphenylmethane with stannous chloride in hydrochloric acid solution. The free base crystallises in yellow scales, melts at 85°, and boils above 360° without decomposition.

Parabenzyl-α-quinoline, $C_{16}H_{13}N$, is prepared from paramidodiphenylmethane by means of Skraup's reaction; it melts at 80·5°, boils above 360°, and is characterised by the large number of well-crystallised simple and double salts it forms. *Diparadiphenylmethanethiocarbamide*, $CS(NH\cdot C_{13}H_{11})_2$, prepared by the action of carbon bisulphide on amidodiphenylmethane, crystallises in yellow scales and melts at 147°. The sulphur-atom is replaced by oxygen by the action of plumbic oxide. If, however, an excess of amidodiphenylmethane is employed, *triparadiphenylmethaneguanidine*, $C_{40}N_{35}N_3$, is formed, melting point 100°. *Paradiphenylmethanecarbamide*, $NH_2\cdot CO\cdot NH\cdot C_{13}H_{11}$, melting at 160°, is prepared from paramidodiphenylmethane hydrochloride by the action of potassium cyanate. The *disubstituted carbamide*, $CO(NH\cdot C_{13}H_{11})_2$, is prepared by the action of carbonyl chloride on the base, or by fusing the last-named carbamide; it melts at 226°. *Ethyl diphenylmethanecarbamate*, $C_{13}H_{11}\cdot NH\cdot COOEt$, melts at 65°, and is prepared by the action of ethyl chlorocarbonate on the base. J. W. L.

Arrangement of Atoms in Space. Part III. Members of the Stilbene-group. By J. WISLICENUS and A. BLANK (*Annalen*, **248**, 1—34).—After referring to the researches of Grimaux, Zinin, Goldenberg, Zagoumenny, Limpricht, and others, on the action of reducing agents on benzoïn, the authors state the results of their own experiments on the action of zinc-dust and acetic acid on an alcoholic solution of benzoïn. The yield of deoxybenzoïn diminishes if the reduction is carried on for more than three hours; the amount of deoxybenzoïnpinacone increases. Small quantities of stilbene are formed, together with a substance crystallising in needles and melting at 172°, which proves to be β-deoxybenzoïnpinacone. Both the α- and β-pinacones decompose on distillation, yielding phenyl benzyl ketone and phenyl benzyl carbinol. The pinacones are optically inactive and probably stand in the same relation to each other as mesotartaric and racemic acids.

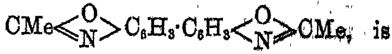
Wislicenus suggests the formula  $\begin{matrix}\text{Ph·C·Cl}\\ \|\\ \text{Ph·C·Cl}\end{matrix}$ for α-tolane dichloride, melting at 143°, and  $\begin{matrix}\text{Ph·C·Cl}\\ \|\\ \text{Cl·C·Ph}\end{matrix}$ for β-tolane dichloride, which melts at 63°. A determination of the molecular weight by Raoult's method, and the vapour-density, show that the substances are isomeric. When tolane tetrachloride is reduced by zinc, the yield of α-tolane dichloride is increased and that of the β-dichloride diminished, by raising the temperature from 20° to 80° or 130°.

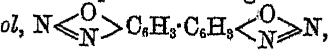
Ditolane hexachloride, $CPhCl_2·CPhCl·CPhCl·CPhCl_2$, is formed by dissolving tolane tetrachloride and α-dichloride in molecular proportion in boiling alcohol; on cooling, the hexachloride is deposited in rhombic plates, soluble in benzene; it melts at 150°. Although Raoult's method gives 266 as the molecular weight of this compound instead of 568·4, the authors regard it as a definite compound, and not as a mixture of the di- and tetra-chlorides, as it is formed by the action of chlorine on a mixture of the α- and β-dichlorides.

β-Dichlorotolane will not unite directly with the tetrachloride to form the hexachloride. W. C. W.

Nitroparadiphenols. By E. KUNZE (*Ber.*, **21**, 3331—3335).—*Metadinitroparadiphenol*, $[(NO_2)_2 : (OH)_2 = 3 : 3' : 4 : 4']$, is formed when the calculated quantity of nitric acid, of sp. gr. 1·45, is added to paradiphenol in glacial acetic acid solution. It separates from glacial acetic acid in brown needles or nodular crystals melting at 272°.

Metadiamidoparadiphenol, $[(NH_2)_2 : (OH)_2 = 3 : 3' : 4 : 4']$, crystallises in colourless plates, decomposes when heated, and dissolves in alcoholic ammonia with a green coloration. The *hydrochloride*, $C_{12}H_6(OH)_2(NH_2)_2,2HCl$, crystallises in colourless needles. The *acetyl*-derivative, $C_{12}H_8N_2O_2Ac_4$, crystallises in colourless needles and melts at 225°.

Diethenyldiamidodiphenol,  $CMe\lessgtr\overset{O}{\underset{N}{}}\gtrless C_6H_3·C_6H_3\lessgtr\overset{O}{\underset{N}{}}\gtrless CMe$, is obtained when the acetyl-derivative is heated above its melting point. It crystallises in colourless prisms melting at 193°.

Tetrazodiphenol,  $N\lessgtr\overset{O}{\underset{N}{}}\gtrless C_6H_3·C_6H_3\lessgtr\overset{O}{\underset{N}{}}\gtrless N$, obtained by diazotising the diamidodiphenol, dissolves in hydrochloric acid with a red coloration, but is reprecipitated unchanged when ammonia is gradually added to the solution.

Diphenoldihydrazine hydrochloride, $[(N_2H_3)_2 : (OH) = 3 : 3' : 4 : 4']$, prepared by reducing the tetrazo-compound with stannous chloride and hydrochloric acid, crystallises in slender needles. When ammonia is added to the aqueous solution, the free *base* is precipitated in colourless crystals; it melts at 140° with decomposition, and reduces Fehling's and ammoniacal silver solutions.

Diacetonediphenoldihydrazone, $C_{18}H_{22}N_4O_2$, is obtained when acetone is added to an aqueous solution of the dihydrazine hydrochloride until the mixture commences to become turbid. It crystallises in colourless rhombic plates, melts at 200°, and is readily soluble in soda, but only sparingly in ammonia, and insoluble in alcohol and ether. Analogous condensation-products are obtained with ethyl acetoacetate, pyruvic acid, benzaldehyde and salicylaldehyde.

The tetranitrodiphenol, which is formed when paradiphenol or metadinitroparadiphenol is nitrated in glacial acetic solution, or when benzidine is treated with nitric acid (compare Caro; Griess and Schmidt; Schultz, Abstract, 1881, 909), has the constitution $[(NO_2)_4 : (OH)_2 = 3 : 3' : 5 : 5' : 4 : 4']$. It yields *tetramidoparadiphenol* when reduced with tin and hydrochloric acid.

Tetramidoparadiphenol crystallises in colourless needles, and decomposes, but does not melt when heated. It oxidises very readily, turns blue on exposure to the air, and is converted into a brownish-black crystalline compound, $C_{12}H_{12}N_4O_2$, when a stream of air is passed for a long time through an ammoniacal alcoholic solution. F. S. K.

New Method of Formation of Benzhydrol-derivatives By K. Albrecht (*Ber.*, **21**, 3292—3299).—*Dimethylamidobenzhydrol*, $OH{\cdot}CHPh{\cdot}C_6H_4{\cdot}NMe_2$, can be obtained by heating a mixture of benzaldehyde (1 mol.) and dimethylaniline (1 mol.) with 20 times its weight of concentrated hydrochloric acid at 100° for 50 hours, neutralising the solution, distilling the unchanged compounds with steam, and recrystallising the residue first from alcohol and then from light petroleum. It can also be prepared by reducing dimethylamidobenzophenone with sodium amalgam in alcoholic solution. It crystallises in slender needles, melts at 69—70°, and is very readily soluble in most solvents, but only moderately so in light petroleum, and insoluble in water. It dissolves in acids, yielding colourless solutions which become yellow when warmed. It is converted into leucomalachite-green when heated with dimethylaniline and zinc chloride.

Paranitrodimethylamidobenzhydrol, $NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NMe_2$, is prepared by heating a mixture of paranitrobenzaldehyde (151 grams), dimethylaniline (121 grams), and hydrochloric acid (3 kilos.) for 40 hours, neutralising the filtered solution, washing the precipitate, and separating the dimethylaniline by distilling with steam. The yield is 80 per cent. of the theoretical. It crystallises from dilute alcohol in slender, yellow needles, melts at 96°, and is very readily soluble in most ordinary solvents, but insoluble in water and light petroleum. The cold acid solutions are colourless but turn yellow when heated. It yields paranitroleucomalachite-green (m. p. 176—177°) when warmed with dimethylaniline and zinc chloride, and when treated with alkaline reducing agents it is converted into the corresponding azoxy-, azo-, and hydrazo-compounds. When heated with methyl iodide in methyl alcoholic solution, a colourless, crystalline compound, probably the *methiodide*, is obtained: it melts at about 175° with liberation of methyl iodide. The salts are all very readily soluble and difficult to obtain crystalline. The *platinochloride*, $(C_{15}H_{16}N_2O_3)_2,H_2PtCl_6$, crystallises in needles and is decomposed by boiling water.

Dimethyldiamidobenzhydrol, $NH_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NMe_2$, prepared by reducing paranitrodimethylamidobenzhydrol with zinc and hydrochloric acid, melts at 165°, and loses 1 mol. H_2O when heated above its melting point. It dissolves in acetic acid with a blue coloration, and crystallises from benzene in shining needles containing benzene, which melt and lose their benzene at 142°. It yields tetramethylparaleucaniline when condensed with dimethylaniline.

The leuco-bases obtained by the condensation of dimethyldiamidobenzhydrol with other aromatic bases yield reddish-violet or blue dyes, whereas those obtained from paranitrodimethylamidobenzhydrol yield greenish colouring matters.

Dimethyldiamidodiphenylmethane, $NH_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2$, is obtained by boiling paranitrodimethylamidobenzhydrol or the corresponding diamido-derivative with zinc and hydrochloric acid. It is a colourless, crystalline compound, melts at 93°, and gives a bluish-violet coloration with chloranil or lead peroxide but not with acids.

The condensation of paranitrobenzaldehyde and dimethylaniline is best effected by dilute hydrochloric acid or dilute sulphuric acid; the hydrol formation only takes place in presence of excess of acid; if alcohol is also present, the ethyl ether is produced. When only a small quantity of acid is employed or if it is very dilute, nitroleucomalachite-green is formed. Hydrols are not formed, or only in very small quantities when phosphoric acid, acid salts, or organic acids are employed, and with excess of concentrated sulphuric acid the only product is tetramethylbenzidine, which is obtained in small quantities.

Dimethylaniline, diethylaniline, methylaniline, and ethylaniline, on the one hand, and paranitro- and metanitro-benzaldehyde on the other hand, condense without difficulty, and the hydrols formed resemble paranitrodimethylamidobenzhydrol.

The ethyl compounds melt at a lower temperature than the corresponding methyl-derivatives; the dialkylhydrols melt at a lower temperature than the monalkyl-derivatives, and the para-compounds at a higher temperature than the isomeric meta-bases. Aniline also combines with paranitrobenzaldehyde, but not so readily as the secondary and tertiary bases.

The amidohydrols dissolve in cold mineral acids and in dilute acetic acid, yielding colourless or only slightly coloured solutions; the diamido-derivatives behave in like manner towards excess of concentrated mineral acids, but dissolve in acetic acid, forming deep blue solutions especially on warming. The diamido-derivatives also give blue solutions when an insufficient quantity of mineral acid is added, or when dilute, only slightly acid solutions are warmed.

The author finds that tetramethyldiamidobenzhydrol does not dissolve in alcohol with a blue coloration as stated by Michler and Dupertius (this Journal, 1877, ii, 333), but that it dissolves in all neutral solvents, forming colourless solutions. F. S. K.

Formation of Benzamarone. By F. R. JAPP and F. KLINGEMANN (*Ber.*, **21**, 2934—2936).—Benzamarone is formed when deoxybenzoïn and benzaldehyde (each 5 grams) are dissolved in cold alcohol, treated with an alcoholic solution of potash (2 grams), and kept over night. The yield is 5 grams. A small quantity of the compound was also obtained by keeping a mixture of benzil, deoxybenzoïn, and weak alcoholic potash for some days in a closed vessel; in this case the benzaldehyde necessary for its formation is produced, together with benzoic acid (which was found in the product) by the slow decomposition of the benzil. Benzamarone, prepared as described above, or by Zinin's method (this Journal, 1871, 539), melts at 214—215° (not 225°). Its mode of formation points to the formula $C_{35}H_{28}O_2$ rather than to the double formula (Knoevenagel, *Ber.*, **21**, 1356).

N. H. M.

Constitution of certain Dichloronaphthalenes. By H. ERDMANN (*Ber.*, **21**, 3444—3448).—*Orthoparadichlorophenylparaconic acid* can be prepared by the action of succinic acid on orthoparadichlorobenzaldehyde, and crystallises from water in white scales melting at 164·5—165·5°. On distillation it yields *orthoparadichlorophenylisocrotonic acid*, $C_6H_3Cl_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$ [Cl : Cl : CH = 1 : 3 : 4], which crystallises from carbon bisulphide in white prisms. When this acid is heated for some minutes at its boiling point, it decomposes into *dichloro-α-naphthol*, $C_{10}H_5Cl_2{\cdot}OH$ [Cl : Cl : OH = 1 : 3 : 4′], which crystallises from carbon bisulphide in large prisms melting at 132°. The corresponding *dichloro-α-naphthylamine*, $C_{10}H_5Cl_2{\cdot}NH_2$, can be prepared by heating the dichloro-α-naphthol with aqueous ammonia; it melts at 116—117°, yields a hydrochloride melting at 204—205°, and when diazotised and treated either with alcohol or with stannous chloride and cupric chloride, is converted into 1 : 3 dichloronaphthalene, which crystallises in white needles melting at 60—61°. The author has, therefore, now prepared synthetically the two dichloronaphthalenes melting at about the same temperature, one of which is homo- and the other hetero-nucleal (compare this vol., p. 150). The remainder of the paper is devoted to a reply to Armstrong and Wynne's criticism of the constitution assigned by Erdmann and Kirchhoff (*loc. cit.*) to the heteronucleal dichloronaphthalenes melting at 48° and at about 61·5° (Proc., 1888, 104).

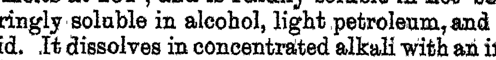
W. P. W.

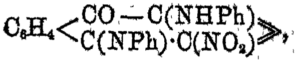
Note by Abstractor.—The author puts forward as original the discovery of the existence of two isomeric dichloronaphthalenes melting at about 61°; a reply to this and other claims in the paper has been published in the Proceedings, 1889, p. 5.

W. P. W.

Action of Chlorine on Phenols. Part III. β-Naphthol. By T. ZINCKE and O. KEGEL (*Ber.*, **21**, 3378—3390, 3540—3559; compare Abstr., 1888, 708).—Cleve has described the preparation of chloro-β-naphthol [Cl : OH = 1 : 2] by the action of chlorine on β-naphthol in acetic acid solution (Abstr., 1888, 597). Experiments show that dichloro-β-ketonaphthalene is simultaneously formed, and the best method of obtaining the chloro-β-naphthol consists in treating the β-naphthol dissolved in acetic acid with a slight excess of chlorine, and reducing the dichloro-β-ketonaphthalene formed by addition of an excess of concentrated stannous chloride. The *acetyl* compound, $C_{10}H_6Cl{\cdot}OAc$, crystallises in thick, colourless, oblique-angled tables, melts at 42—43°, and is very soluble in alcohol.

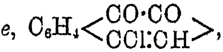
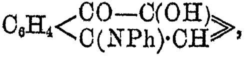
αβ-Dichloro-β-naphthol, $C_{10}H_5Cl_2{\cdot}OH$ [Cl : OH : Cl = 1 : 2 : 3], can be obtained by the reduction of tetrachloro-β-ketohydronaphthalene (see below), but when prepared from this source is always mixed with a larger or smaller quantity of the isomeric αα-dichloro-β-naphthol. It is best prepared, however, by reducing trichloro-β-ketonaphthalene dissolved in acetic acid, either with stannous chloride or a sulphite. It crystallises in aggregates of slender, lustrous needles, melts at 80—81°, and is readily soluble in alcohol, ether, benzene, and acetic acid. The *acetyl*-derivative, $C_{10}H_5Cl_2{\cdot}OAc$, crystallises in flat, rhombic tables showing a peculiar striation on some of the faces, melts at 79—80°, and is readily soluble in alcohol and acetic acid. When treated with chlorine in acetic acid solution, αβ-dichloro-β-naphthol is converted into β-trichloro-β-ketonaphthalene, which by further addition of chlorine forms β-pentachloro-β-ketohydronaphthalene. Chromic acid converts it into a yellow, amorphous substance, probably a diquinone-derivative, but on careful oxidation with nitric acid (sp. gr. = 1·4), it yields chloro-β-naphthaquinone as chief product, a second quinone-like compound, probably an αβ-nitrochloro-β-naphthaquinone, being simultaneously formed, which melts at 172°, and is characterised by dissolving in aqueous alkali with an intense bluish-green colour, and in alcoholic alkali with a deep blue colour.

αα-Dichloro-β-naphthol, $C_{10}H_5Cl_2{\cdot}OH$ [Cl : OH : Cl = 1 : 2 : 4], is obtained, together with the αβ-derivative, by the reduction of tetrachloro-β-ketohydronaphthalene with stannous chloride in the cold, and is separated from its isomeride by repeated crystallisation from light petroleum. It crystallises in long, hard, white, asbestos-like needles, melts at 123—124°, and is readily soluble in ether, alcohol, and acetic acid. Its *acetyl*-derivative, $C_{10}H_5Cl_2{\cdot}OAc$, crystallises in small, colourless needles, and melts at 90—91°. On treatment of its acetic acid solution with the calculated quantity of chlorine, it is converted into α-trichloro-β-ketonaphthalene, which by the further action of chlorine yields α-pentachloro-β-ketohydronaphthalene (?). When oxidised with chromic acid, it is converted into a yellow, amorphous substance, whilst with nitric acid (sp. gr. = 1·4), it yields as chief product αβ-chloronitro-β-naphthaquinone, α-chloro-β-naphthaquinone being formed simultaneously in very small quantities. *αβ-Chloronitro-β-naphthaquinone*,  $C_6H_4<\begin{matrix}CO{\cdot}CO\text{———}\\CCl{:}C(NO_2)\end{matrix}>$, crystallises in red or brownish-red needles, melts at 184°, and is readily soluble in hot benzene or acetic acid, sparingly soluble in alcohol, light petroleum, and cold benzene or acetic acid. It dissolves in concentrated alkali with an intense greenish-blue, and in dilute alkali with a reddish-brown colour. When treated with aniline, it yields *anilidonitronaphthaquinone anilide*,



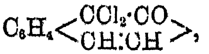
$$C_6H_4<\begin{matrix}CO-C(NHPh)\\C(NPh){\cdot}C(NO_2)\end{matrix}\gg,$$

which crystallises in dark violet scales showing a metallic lustre, melts at 249—250°, and is insoluble in alkalis, sparingly soluble in acetic acid and benzene, but more soluble in toluene. The salts of this base are decomposed by alcohol or acetic acid unless acid is present, when they dissolve with a violet colour.

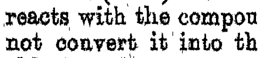
α-Chloro-β-naphthaquinone,

$C_6H_4<\begin{matrix}CO\cdot CO\\ CCl{:}CH\end{matrix}>$,
crystallises in reddish-brown, strongly dichroic needles, melts at 136°, and yields *β-hydroxynaphthaquinone anilide*,

$C_6H_4<\begin{matrix}CO—C(OH)\\ C(NPh)\cdot CH\end{matrix}\gg$,
on treatment with aniline.

Trichloro-β-naphthol, $C_{10}H_4Cl_3\cdot OH$ [Cl : OH : Cl : Cl = 1 : 2 : 3 : 4], is obtained by the reduction of β-pentachloro-β-ketohydronaphthalene with stannous chloride or sodium sulphite. It crystallises in colourless needles, melts at 162°, and is less soluble than the dichlorinated derivatives. Its *acetyl*-compound, $C_{10}H_4Cl_3\cdot OAc$, crystallises from acetic acid in white, lustrous needles and melts at 133·5—134°. On treatment in acetic acid solution with chlorine, it is converted into tetrachloro-β-ketonaphthalene. Chromic acid oxidises it to a yellow, amorphous substance, containing probably a diquinone, whilst nitric acid (sp. gr. = 1·4) converts it into αβ-dichloro-β-naphthaquinone.

α-Dichloro-β-ketonaphthalene (*β-naphthaquinone chloride*),

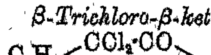


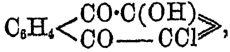
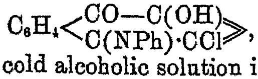
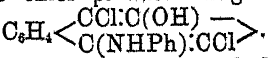
$$C_6H_4<\begin{matrix}CCl_2\cdot CO\\ CH{:}CH\end{matrix}>,$$

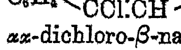
is obtained by treating chloro-β-naphthol or β-naphthol dissolved in acetic acid or chloroform with the calculated quantity of chlorine. It is a liquid, and rapidly decomposes on distillation in a vacuum. When treated with aniline, it is converted into β-hydroxynaphthaquinone anilide if dissolved in alcohol, but into anilidonaphthaquinone anilide,

$C_6H_4<\begin{matrix}CO\cdot C(NHPh)\\ C(NPh)—CH\end{matrix}\gg$,
if dissolved in acetic acid. Phenylhydrazine reacts with the compound in a peculiar manner, inasmuch as it does not convert it into the so-called benzeneazo-β-naphthol, but into a chlorinated azo-compound, *β-benzeneazo-α-chloronaphthalene*,

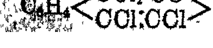
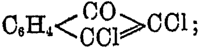
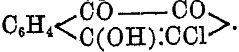
$$C_{10}H_6Cl\cdot N{:}NPh\ [Cl : N_2Ph = 1 : 2],$$

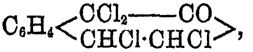
which crystallises in slender, reddish or pale-orange needles, melts at 115°, is readily soluble in alcohol, benzene, and acetic acid, and on reduction in acetic acid solution with stannous chloride yields not chloro-β-naphthylamine but a basic compound free from chlorine. A mixture of brown substances is formed by the action of hydroxylamine on dichloro-β-ketonaphthalene.

β-Trichloro-β-ketonaphthalene (*β-chloro-β-naphthaquinone chloride*),

$C_6H_4<\begin{matrix}CCl_2\cdot CO\\ CH{:}CCl\end{matrix}>$,
is formed by withdrawing the elements of hydrogen chloride from tetrachloro-β-ketohydronaphthalene. It is not, however, necessary to first prepare this compound in the pure state, since the product obtained by treating a well-cooled 10 to 12 per cent. solution of β-naphthol in acetic acid with an excess of chlorine, readily evolves hydrogen chloride when poured into an equal volume of alcohol,

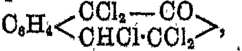
and yields the trichloroketone. It crystallises from alcohol or acetic acid in thick, yellow needles, which darken in colour on exposure to light and melt at 95—96°; whilst from ether it separates in large, monoclinic prisms, which show, however, a marked rhombic habit if the solution is impure. When finely powdered, it dissolves slowly in dilute alkali, and yields, in addition to brown, resinous substances, ββ-chlorhydroxynaphthaquinone, $C_6H_4<\begin{matrix}CO\cdot C(OH)\\CO — CCl\end{matrix}>$, whose formation is accounted for by supposing that the β-chloro-α-hydroxy-β-naphthaquinone, which would most probably be formed in the first instance, undergoes isomeric change. When heated either with dilute alcohol or with dilute acetic acid, it forms resinous compounds, together with some chlorhydroxynaphthaquinone and a compound which crystallises in needles and seems to be a dichloro-β-naphthol. Stannous chloride and sulphites reduce it to αβ-dichloro-β-naphthol; phenylhydrazine in alcoholic solution reduces it, hydroxylamine converts it into resinous products and orthotoluylenediamine reacts with it, forming crystalline compounds. When the hot alcoholic or acetic acid solution of the trichloroketone is treated with aniline, *ββ-chlorhydroxynaphthaquinone anilide*, $C_6H_4<\begin{matrix}CO—C(OH)\\C(NPh)\cdot CCl\end{matrix}>$, is obtained, melting at 253°; if, however, a cold alcoholic solution is used this compound is formed only in relatively small quantities, the chief product being *αβ-dichloro-β-hydroxy-α-naphthylphenylamine*, $C_6H_4<\begin{matrix}CCl{:}C(OH) —\\C(NHPh){:}CCl\end{matrix}>$. This crystallises from chloroform in colourless, transparent, hard, thick crystals, from acetic acid in slender, lustrous needles, and from a mixture of ether and light petroleum in large prisms, melts at 162°, and dissolves without decomposition in alkalis. Its *acetyl*-derivative, $C_{16}H_{10}NCl_2\cdot OAc$, crystallises from alcohol or acetic acid in small, lustrous prisms, and melts at 164°. In one preparation of this compound, a third substance was once obtained, which crystallised in small, white scales, melted at 223°, and gave results on analysis indicating it to be a chlorhydroxydiphenylnaphthylenediamine.

α-Trichloro-β-ketonaphthalene (*α-chloro-β-naphthaquinone chloride*), $C_6H_4<\begin{matrix}CCl_2\cdot CO\\CCl{:}CH\end{matrix}>$, is prepared by treating an acetic acid solution of αα-dichloro-β-naphthol with the calculated quantity of chlorine. It crystallises from light petroleum in thick, white needles, and from a mixture of ether and benzene in well-formed, transparent, rhombic prisms, melts at 86—87°, and is readily soluble in hot alcohol, benzene, ether, and acetic acid. On treatment with alkali, it yields β-hydroxynaphthaquinone; aniline converts it in alcoholic solution into β-hydroxynaphthaquinone anilide, and in acetic acid solution into anilidonaphthaquinone anilide; stannous chloride reduces it to αα-dichloro-β-naphthol, and hydroxylamine reacts with it, forming an oxime.

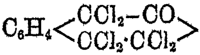
Tetrachloro-β-ketonaphthalene (*dichloro-β-naphthaquinone chloride*), $C_6H_4<\begin{matrix}CCl_2\cdot CO\\CCl{:}CCl\end{matrix}>$, is obtained by suspending trichloro-β-naphthol in acetic acid, and passing chlorine until the whole has gone into solution and the liquid has a distinct odour of the gas. It crystallises from alcohol or acetic acid in yellowish scales, and melts at 96—97°. When treated with concentrated alkali, it yields dichlorhydroxyindenecarboxylic acid, which can be recognised by transforming it into dichloroketoindene,  $C_6H_4<\substack{CO\\CCl}>CCl$; alcoholic potash, on the other hand, converts it into the supposed ethyl-derivative of chlorhydroxy-β-naphthaquinone,  $C_6H_4<\substack{CO——CO\\C(OH):CCl}>$. Aniline reacts with it, forming ββ-chlorhydroxynaphthaquinone anilide.

Tetrachloro-β-ketohydronaphthalene,  $C_6H_4<\substack{CCl_2——CO\\CHCl\cdot CHCl}>$, is the most easily prepared of all the keto-derivatives of β-naphthol, and is obtained by treating a carefully cooled solution of β-naphthol in acetic acid with an excess of chlorine, and at once precipitating the product with water. It is necessary that the chlorination should be completed in one operation, since a partially chlorinated solution, after remaining 12 hours, gave on further chlorination a crystalline separation consisting of thick, yellowish needles, which had the composition $(C_{10}H_6Cl_2O)_n$, melted at 193°, and were sparingly soluble in most solvents. Obtained in this way, the tetrachlorhydroketone crystallises with 1 mol. H_2O in white, lustrous scales, melts at 90—91°, and is converted into the anhydrous form by repeated crystallisation from light petroleum; it then crystallises in white, lustrous scales melting at 102—103°, white needles melting at 101—102°, or, occasionally, in colourless, monoclinic prisms. It dissolves in cold alcohol, but on standing, or more rapidly on warming, it undergoes conversion into β-trichloro-β-ketonaphthalene. Stannous chloride and sulphites reduce it to αβ-dichloro-β-naphthol on warming, and to a mixture of this with the αα-derivative in the cold; solution of sodium carbonate converts it into β-chloro-β-naphthaquinone; aqueous soda dissolves it with the formation of ββ-chlorhydroxynaphthaquinone, and aniline reacts with it as with β-trichloro-β-ketonaphthalene.

When α-trichloro-β-ketonaphthalene is further chlorinated, it yields a compound crystallising in small forms, which resemble rhombic sulphur crystals both in colour and shape. Although this compound always shows the same melting point, it is very probable that it is a mixture of tetrachloro-β-ketonaphthalene and hexachloro-β-ketonaphthalene in molecular proportions, which cannot be separated by crystallisation, and not α-pentachloro-β-ketohydronaphthalene, inasmuch as a portion of the finely powdered substance dissolved rapidly in alkali, yielding a solution in which dichlorhydroxyindenecarboxylic acid could be detected, whilst the residue was white, and resembled hexachloro-β-ketohydronaphthalene in its properties.

β-Pentachloro-β-ketohydronaphthalene,  $C_6H_4<\substack{CCl_2—CO\\CHCl\cdot CCl_2}>$, is obtained by saturating a solution of β-trichloro-β-ketonaphthalene in acetic acid with chlorine. It crystallises in well-formed, colourless, triclinic prisms, which melt at 116—117°; if crystallised from ether, however, it forms very large and apparently rhombohedral crystals, and when crystallised from benzene yields both transparent forms and crystals which effloresce on exposure to the air. On reduction with stannous chloride, sodium sulphite, or less readily with phenylhydrazine, it is converted into trichloro-β-naphthol, and only reacts with aniline at the boiling point, when it yields ββ-chlorohydroxynaphthaquinone anilide. When treated in alcoholic solution with 25 per cent. aqueous potash, the ring is split, and *orthodichlorovinyldichlorobenzylcarboxylic acid*, $C_2HCl_2{\cdot}C_6H_4{\cdot}CCl_2{\cdot}COOH$, is obtained, which crystallises from chloroform in transparent, lustrous forms, and from light petroleum in thick, white needles, melts at 130—131° with decomposition and evolution of hydrogen chloride, but not of carbonic anhydride, and is readily soluble in the ordinary solvents. It dissolves in aqueous sodium carbonate without decomposition, but is slowly converted into the corresponding benzoylcarboxylic acid by caustic alkalis. On oxidation, it yields dichlorovinylbenzoic acid. The *methyl* salt, $C_9H_5Cl_4{\cdot}COOMe$, crystallises in slender, white needles, melts at 99—100°, and is readily soluble in alcohol and ether.

Orthodichlorovinylbenzoylcarboxylic acid, $C_2HCl_2{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$, is prepared by dissolving the finely-powdered pentachloroketone in 25 per cent. aqueous potash and acidifying. It crystallises from dilute alcohol in long, slender, yellowish needles, melts without decomposition at 106—107°, and is readily soluble in alcohol and acetic acid, but only sparingly in light petroleum. The *methyl* salt has not been solidified, and no solid compound could be obtained by the action of hydroxylamine.

Hexachloro-β-ketonaphthalene,  $C_6H_4{<}\begin{matrix}CCl_2{-}CO\\CCl_2{\cdot}CCl_2\end{matrix}{>}$, is prepared by heating the tetrachloroketone with 1 part of manganese dioxide and 5 parts of fuming hydrochloric acid (sp. gr. = 1·19) at 140—150° for 6 to 8 hours. It crystallises in long, colourless, prismatic needles or in compact, seemingly monoclinic, and occasionally tabular crystals, melts at 129°, and dissolves in ether, benzene, hot alcohol, and hot acetic acid. On reduction, it is converted into trichloro-β-naphthol. When treated in warm alcoholic solution with concentrated aqueous potash, the ring is split, and *orthotrichlorovinyldichlorobenzylcarboxylic acid*, $C_2Cl_3{\cdot}C_6H_4{\cdot}CCl_2{\cdot}COOH$, can be obtained from the solution by saturating it with hydrochloric acid. It crystallises in colourless needles or long, thick tables, melts at 150° with decomposition, and is readily soluble in alcohol and ether. On oxidation, it yields orthotrichlorovinylbenzoic acid. The *methyl* salt, $C_9H_4Cl_5{\cdot}COOMe$, crystallises in colourless, slender needles, and melts at 83—84°. When the acid is dissolved in concentrated aqueous soda and afterwards acidified, an oil is obtained which could not be crystallised, and probably consists of the corresponding ketonic acid.

W. P. W.

Reduction Products of the Azo-dyes of the Naphthalene Series. By O. N. WITT (*Ber.*, 21, 3468—3489).—The azo-dyes obtained by the action of diazotised bases on the isomeric mono- and di-sulphonic acids of α- and β-naphthol and naphthylamine are converted by reduction into two amines, one being the base from which the diazo-compound was obtained, and the second being the amido-compound of the naphthalene-derivative employed. The actual or supposed instability of these reduction products has hitherto led to the neglect of this method of determining the constituents of the naphthalene azo-dyes, but this instability is to be ascribed to the secondary action of the reducing agent employed, the use of alkaline reducing agents such as zinc-dust with ammonia or soda, or the addition of alkali to the reduction product, leading in all cases to decomposition. The method, however, is the only one capable of giving trustworthy results, and experiment shows that with a suitable reducing agent, a solution of "tin salt" in hydrochloric acid, the reduction products of the naphthalene azo-dyes can be isolated for subsequent identification. For analytical purposes, 1 gram of the azo-dye, freed from dextrin, sodium sulphate, and like impurities, is dissolved in 10 c.c., or in the case of the less soluble dyes 20 c.c. of boiling water, the source of heat is then removed, and 6 c c. of a solution of 40 grams of "tin salt" in 100 c.c. of pure hydrochloric acid (sp. gr. = 1·19), corresponding to 2 grams of tin salt, is added. The amidonaphthol- or naphthalenediamine-sulphonic acid formed may separate from the warm or cold solution, or not at all, according to the nature of the substance, and in the last case precipitation with sodium acetate, salt, or hydrochloric acid, as determined by experiment, must be resorted to. This process is termed by the author a normal reduction.

In order to isolate and characterise the reduction products, the aniline-azo-dyes derived from β-naphthol, β-naphthylamine, and their mono- and di-sulphonic acids were alone employed, but the method presents no difficulties when applied to those azo-dyes found in commerce which are derivatives of these naphthalene-compounds.

Derivatives of β-Naphthol.—The azo-dyes derived from β-naphthol are known to give amido-β-naphthol on reduction (Liebermann, *Ber.*, **14**, 1310). β-Naphthol-orange (mandarin) on normal reduction yields a clear and colourless solution from which white needles and stellar aggregates of amido-β-naphthol hydrochloride separate on cooling. This salt dissolves readily in hot water, but cannot be precipitated either by alkalis or soda, the solution becoming dark brown in colour. Sodium acetate, however, precipitates amido-β-naphthol from the solution in lustrous scales, which dissolve readily in ether, and crystallise in small, quadratic tables on spontaneous evaporation of the solvent. The addition of ferric chloride to the hydrochloride in aqueous solution converts it into β-naphthaquinone.

Derivatives of the β-Naphtholsulphonic Acids.—(1.) *Amido-β-naphthol-α-sulphonic acid*, $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H$.—The orange from diazobenzene chloride and Bayer's β-naphthol-α-sulphonic acid on normal reduction yields amidonaphtholsulphonic acid, which crystallises from the hot solution in small, well-formed, rectangularly striated, pale rose-coloured scales, and can be purified by recrystallisation from a dilute solution of sodium acetate. It is very sparingly soluble in hot water and in sodium acetate solution; alkalis and alkaline earths, however, dissolve it readily, and the solutions very rapidly become deep orange-brown on exposure to air. Oxidising agents colour both the neutral and alkaline solutions of the acid deep yellow or brown, and silver salts are at once reduced by it and each of the following acids in both acid and ammoniacal solution. It does not yield a diazo-compound on treatment in acid solution with sodium nitrite, and diazo-compounds do not react with it, but decompose with the evolution of nitrogen and formation of a brown colour. When treated with nitrosodimethylaniline hydrochloride in a 50 per cent. acetic acid solution, it forms a characteristic violet colouring matter which in aqueous solution is coloured red on addition of aqueous soda.

(2.) *Amido-β-naphthol-β-sulphonic Acid* (Meldola, Trans., 1881, 47; Griess, Abstr., 1882, 50).—The orange from diazobenzene chloride and Schäffer's β-naphthol-β-sulphonic acid on normal reduction yields this amido-acid which separates from the hot solution as a crystalline magma. It is insoluble in alcohol, and cannot be purified by solution in water since decomposition ensues with the formation of brown solutions, which on the addition of hydrochloric acid become violet. It is soluble in hot 20 per cent. aqueous sodium acetate in the presence of acetic acid, and is precipitated from the solution on addition of hydrochloric or dilute sulphuric acid. With oxidising agents and sodium nitrite, it behaves like the preceding compound, but differs from it in not yielding a colouring matter with nitrosodimethylaniline hydrochloride. It is characterised by readily yielding, on treatment with diazo-compounds, beautiful colouring matters, which, however, do not dye wool; thus with diazobenzenesulphonic acid a magenta colouring matter is obtained whose shade is rendered bluish on addition of hydrochloric acid, whilst with tetrazostilbenedisulphonic acid a reddish-violet colouring matter is formed, which on addition of hydrochloric acid is precipitated in beautiful blue flocks soluble in water to a blue solution.

(3.) *Amido-β-naphthol-δ-sulphonic Acid.*—The aniline-azo-derivative of Casella's naphtholsulphonic acid F, on normal reduction, yields this amido-acid, which crystallises from the warm solution in shimmering, rose-red needles. It closely resembles amido-β-naphthol-β-sulphonic acid in its properties and reactions, but is less sensitive, and is characterised by reacting only with some diazo-compounds, and then but slowly. Thus, addition of the diazo-compound from Brönner's β-naphthylamine-β-sulphonic acid results in decomposition and the evolution of nitrogen, whereas amido-β-naphthol-β-sulphonic acid forms with it a reddish-violet colouring matter. Diazobenzenesulphonic acid produces with it a transitory red coloration followed by decomposition and evolution of nitrogen; tetrazostilbenedisulphonic acid, however, reacts with it, forming a dull brownish-violet colouring matter, which is precipitated without change of colour by hydrochloric acid.

(4.) *Amido-β-naphthol-γ-sulphonic Acid.*—The aniline-azo-derivative of β-naphthol-γ-sulphonic acid, on normal reduction, yields this amido-acid, which separates in a crystalline form from the warm solution, and can be purified by repeated solution in hot aqueous sodium acetate and precipitation with hydrochloric acid. It is the most sparingly soluble as well as the most stable of the isomerides, and forms small, rose-red aggregates, which are scarcely soluble in hot water. With alkalis, oxidising agents, and silver salts, it behaves like its isomerides, and is characterised by reacting neither with diazo-compounds nor with nitrosodimethylaniline hydrochloride in acetic acid solution.

Derivatives of β-Naphtholdisulphonic Acids. (1.) *Amido-β-naphthol-α-disulphonic acid.*—"Ponceau 2 G," the aniline-azo-derivative of β-naphthol-α-disulphonic acid (R-acid), on normal reduction yields a clear solution, which after cooling and standing some time deposits slender, snow-white, silky needles; an immediate separation in the form of satiny needles is, however, produced by the addition of an equal volume of saturated salt solution directly the reduction is complete. The *sodium hydrogen* salt of the amido-acid, $NH_2 \cdot C_{10}H_4(OH)(SO_3H) \cdot SO_3Na$, thus obtained, is collected, washed with alcohol and ether and dried, but is still impure, owing to the presence of amido-β-naphthol-β-sulphonic acid obtained from the Schäffer's acid, which is always present in the R-acid employed technically; it can be purified by rapidly dissolving it in 10 times its weight of acidified water, adding an equal volume of ice-cold alcohol, and at once immersing the solution in a freezing mixture in order to bring about rapid crystallisation. In the dry state the compound is stable, but in aqueous solution it is extraordinarily unstable, decomposing at once into what is almost certainly *sodium ammonium dihydroxynaphthalenedisulphonate*, $SO_3Na \cdot C_{10}H_4(OH)_2 \cdot SO_3NH_4$, which separates from the solution on addition of salt in grey scales. This compound is readily soluble in water, less so in alcohol, decomposes rapidly on addition of alkalis with the formation of brown solutions, and is a salt of the supposed amido-β-naphthol-α-disulphonic acid described by Griess (Abstr., *loc. cit.*). The amido-acid is rapidly oxidised by alkalis, does not react with diazo-compounds and nitrosodimethylaniline, and immediately reduces silver salts to metallic silver.

(2.) *Amido-β-naphthol-γ-disulphonic Acid.*—"Orange G", the aniline-azo-derivative of β-naphthol-γ-disulphonic acid (pure G-acid), on normal reduction, yields a clear solution from which salt solution precipitates the *sodium hydrogen* salt of the amido-acid, $NH_2 \cdot C_{10}H_4(OH)(SO_3H) \cdot SO_3Na$, in snow-white prisms or small aggregates of prisms. It is much more stable than its isomeride, and although it shows all the reactions given by the α-derivative, yet the decompositions take place so much more slowly as to afford a means of distinguishing between the two, for example, with silver salts the reduction only commences some minutes after the solutions have been mixed.

Derivatives of β-Naphthylamine.—The azo-dyes derived from β-naphthylamine are known to give α-β-orthonaphthylenediamine on reduction. The aniline-azo-derivative formed by the action of diazobenzenesulphonic acid on β-naphthylamine, on normal reduction yields the hydrochloride of this diamine which crystallises from the warm solution in slender, white needles, and is characterised by forming naphthaphenanthrazine when treated in aqueous solution containing acetic acid and sodium acetate with an aqueous solution of the bisulphite compound of phenanthraquinone. Naphthaphenanthrazine crystallises in yellowish-white, sparingly soluble needles, and dissolves in sulphuric acid with a blackish-violet colour, which becomes yellow on dilution. The azo-dyes obtained from phenyl-β-naphthylamine and the toluyl-β-naphthylamines have already been shown to yield azines on treatment with acids (Abstr., 1887, 590).

Derivatives of β-Naphthylaminesulphonic Acids.—(1.) The β-naphthylamine-α-sulphonic acid (Badische acid) reacts with diazobenzenesulphonic acid, but yields a yellow diazoamido- and not an azo-compound, which on normal reduction is converted into phenylhydrazine and unchanged Badische acid.

(2.) *Orthonaphthylenediamine-β-sulphonic acid*, $C_{10}H_5(NH_2)_2 \cdot SO_3H$.—"Gold brown," the aniline-azo-derivative of β-naphthylamine-β-sulphonic acid (Brönner's acid), on normal reduction, yields crystals which separate from the hot solution, and can be purified by solution in aqueous sodium acetate and precipitation with acetic or hydrochloric acids. It forms slender, pointed needles, is very sparingly soluble in water, and in alkaline solution becomes rapidly brown on exposure to the air; an excess of soda, however, precipitates a sodium salt in silvery scales. Potassium ferricyanide produces a brown colour with the alkaline solution, which subsequently changes to a pure yellow, and ferric chloride forms a dull green precipitate in the aqueous solution. The acid is characterised by yielding the citron-yellow *sodium naphthaphenanthrazinesulphonate*, $C_{24}H_{13}N_2 \cdot SO_3Na$, when its solution in sodium acetate and acetic acid is treated with an aqueous solution of the bisulphite compound of phenanthraquinone. This salt dissolves in sulphuric acid with a reddish-violet colour, and on fusion with potassium hydroxide is converted into a *eurhodol*, which is obtained in brown, gelatinous flocks on acidifying the solution of the melt, dissolves in sulphuric acid with a pure ultramarine colour, and is slowly precipitated as a cherry-red sulphate on addition of water to the solution.

(3.) *Orthonaphthylenediamine-δ-sulphonic Acid.*—The aniline-azo-dye obtained from β-naphthylamine-δ-sulphonic acid (F-acid), on normal reduction yields a clear solution which deposits only a few flocks on standing. An indistinctly crystalline precipitate is obtained by adding salt solution and hydrochloric acid, and this, when purified by solution in sodium acetate and precipitation with hydrochloric acid, forms a grey powder which dissolves in water more readily than the β-acid. In its behaviour with alkalis, potassium ferricyanide, and ferric chloride, it resembles the β-acid, but excess of soda does not precipitate a crystalline sodium salt from its solution. The corresponding *sodium naphthaphenanthrazinesulphonate* crystallises from dilute alcohol in slender needles and dissolves in sulphuric acid with a reddish-violet colour, and the *eurhodol* forms a pure violet solution with sulphuric acid, which on dilution yields a brownish-red precipitate of the sulphate.

(4.) *Orthonaphthylenediamine-γ-sulphonic Acid.*—The aniline-azo-derivative of β-naphthylamine-γ-sulphonic acid (Dahl's acid) on normal reduction yields this acid, which crystallises from the hot solution, and can be purified by solution in sodium acetate and precipitation with hydrochloric acid. It crystallises in shimmering brown scales, is more soluble in water than the β-compound, reduces silver salts, and in aqueous solution yields a deep green coloration with ferric chloride, the solution subsequently depositing a dark-green precipitate. The alkaline solution slowly assumes a brown colour. The corresponding *sodium naphthaphenanthrazinesulphonate* dissolves in sulphuric acid with a violet colour, which on dilution becomes orange, and the *eurhodol* dissolves in sulphuric acid with a black-violet colour, and the solution on dilution with water first becomes cherry-red, and afterwards deposits the sulphate in dark-red flocks.

Derivatives of β-Naphthylaminedisulphonic Acids.—The β-naphthylamine-γ-disulphonic acid (amido-G-acid), according to Schultz, does not combine with diazo-compounds.

The aniline-azo-derivative of β-naphthylamine-α-disulphonic acid (amido-R-acid), on normal reduction, yields a clear solution on cooling, from which hydrochloric acid precipitates the *sodium hydrogen salt*, $SO_3H \cdot C_{10}H_4(NH_2)_2 \cdot SO_3Na$. This can be purified by dissolving it in water and precipitating with salt solution and fuming hydrochloric acid. When obtained by precipitation with hydrochloric acid, it forms a sandy powder consisting of well formed and often twinned prisms, whilst salt solution precipitates it in the form of slender, pointed needles. It is readily soluble in water, and the solution fluoresces green in the absence of mineral acids, yields sparingly soluble precipitates with barium and calcium chlorides, and becomes coloured deep green on addition of ferric chloride. It resembles orthonaphthylenediamine-γ-sulphonic acid in its behaviour with alkalis and silver salts. The corresponding *sodium naphthaphenanthrazinedisulphonate* forms a transparent, citron-yellow, gelatinous mass which could not be crystallised, and dissolves in sulphuric acid with a very characteristic bluish-magenta coloration, which on dilution becomes first yellow and then orange. The *eurhodol* is insoluble in water and yields a deep greenish-blue solution in sulphuric acid, which on dilution becomes first violet and then bordeaux-red; further dilution precipitates the eurhodol itself in yellowish-brown flocks.

W. P. W.

Constitution of β-Naphthol-α-Sulphonic Acid. By O. N. WITT (*Ber.*, **21**, 3489—3492).—When amido-β-naphthol-α-sulphonic acid (see preceding Abstract) is heated with concentrated hydrochloric acid at 120° for 4—5 hours, it yields a dihydroxynaphthalene, which on oxidation with ferric chloride is converted into β-naphthaquinone. It follows therefore that amido-β-naphthol-α-sulphonic acid has the constitution [$NH_2 : OH : SO_3H = 1 : 2 : ?$], and consequently Bayer's β-naphthol-α-sulphonic acid cannot have the constitution [$SO_3H : OH = 1 : 2$]. W. P. W.

Note by Abstractor.—Throughout the paper the author regards Armstrong as the authority for the 1 : 2 formula hitherto frequently assigned to Bayer's acid; this, however, is due to a misconception (compare Armstrong, Proc., 1889, 8). The acid has been shown to be heteronucleal by Armstrong and Wynne (Proc., 1888, 104; 1889, 7).

W. P. W.

Action of Fuming Sulphuric Acid on Brönner's β-Naphthylamine-β-Sulphonic Acid. By S. FORSLING (*Ber.*, **21**, 3495—3499).

When Brönner's β-naphthylamine-β-sulphonic acid, dried at 160°, is heated with 3 to 4 parts of fuming sulphuric acid at about 110° until a test specimen dissolves in water, a mixture of β-naphthylaminedisulphonic acid, together with a small quantity of a second acid, is obtained; the yield of the latter is increased by allowing the sulphonation to proceed at a higher temperature for a longer time.

β-Naphthylaminedisulphonic acid, $NH_2{\cdot}C_{10}H_5(SO_3H)_2$, cannot be obtained by acidifying the solution of a normal salt, since the corresponding acid salt is thereby formed. It can be prepared, however, by treating the barium salt with sulphuric acid, and crystallises in white needles which are extremely soluble in water, but only sparingly in alcohol. The *potassium* salt crystallises with 2 mols. H_2O in large, yellow crystals; the *potassium hydrogen* salt, with 1 mol. H_2O, in long, white, slender needles; the *sodium* salt in long, white needles; the *sodium hydrogen* salt, with 2 mols. H_2O, in long, white, slender needles; the *ammonium* salt, with 1 mol. H_2O, in large, red, triclinic crystals, and the *ammonium hydrogen* salt in anhydrous, slender, white needles; the *barium* and *calcium* salts are also described. The normal salts are readily soluble in water, the acid salts, on the contrary, are somewhat sparingly soluble in cold water. When diazotised in alcoholic solution with nitrous acid, the acid salts of the acid are converted into the corresponding diazonaphthalenedisulphonates, which are relatively stable, and can be boiled with absolute alcohol without decomposition; the *potassium* and *ammonium* salts crystallise in microscopic, yellow, rhombic tables, the *sodium* salt in needles.

The *potassium* salt of *β-chloronaphthalenedisulphonic acid*,

$$C_{10}H_5Cl(SO_3K)_2 + 5H_2O,$$

is obtained by heating potassium diazonaphthalenedisulphonate with cuprous chloride and hydrochloric acid. It crystallises in white needles, and is only sparingly soluble in cold water. The *disulphochloride*, $C_{10}H_5Cl(SO_2Cl)_2$, crystallises from benzene in thick tables, and from chloroform in small, colourless prisms, melts at 124·5°, and is very sparingly soluble in light petroleum. The *trichloronaphthalene*, $C_{10}H_5Cl_3$, crystallises in dendritic aggregates of slender needles, melts at 91°, and is sparingly soluble in alcohol, but readily soluble in chloroform.

W. P. W.

Filicic Acid. By E. Luck (*Ber.*, **21**, 3465—3468).—A reply to the criticisms of Daccomo (*Ber.*, **21**, 2962, this vol., p. 54). Pure filicic acid melts at 184·5°, but if the specimen is allowed to solidify and the melting point again taken, it is found to sinter at about 130°, and melt at 150—160°.

W. P. W.

Transformation of Terpilene into Menthene. By G. Bouchardat and J. Lafont (*Compt. rend.*, **107**, 916—918).—When terpin is treated with concentrated hydriodic acid, it yields a crystalline terpilene dihydriodide identical with that obtained from terebenthene. The terpin is mixed with hydriodic acid saturated at 0°, and as soon as the temperature is raised, the liquid separates into two layers and iodine is liberated, which indicates that hydrogen has combined with the hydrocarbon. The mixture was heated at 100° for 20 to 24 hours, the weight of hydriodic acid varying from 16 to 60 times that of the terpin. The principal reaction is represented by the equation $C_{10}H_{16},2HI + HI = C_{10}H_{18}HI + I_2$, whilst part of the terpilene is polymerised. The principal product is isomeric if not identical with menthene hydriodide, $C_{10}H_{19}I$, but it cannot be isolated from the accompanying diterpilene, since it decomposes even at a somewhat low temperature.

If the free iodine and acid are removed, and the hydriodide is heated at 100° with potassium acetate, potassium iodide is deposited and an oily liquid is obtained which is lighter than water. When distilled it separates into two fractions, one of which boils at 210—225° under a pressure of 30 mm., and consists of diterpilene mixed with hydrides of similar boiling point, whilst the other has the composition $C_{10}H_{18}$, and boils at 167—170° under ordinary pressure; sp. gr. at 0° = 0·837.

The latter hydrocarbon combines very slowly with hydracids, and differs in this respect from terpilene. If heated at 100° for 10 hours with 6 to 8 volumes of hydrochloric acid saturated at 0°, combination is complete, but only a monohydrochloride is formed. This is an oily liquid, lighter than water. It has an agreeable odour, does not solidify at −60°, and boils without decomposition at 105—110° under a pressure of 30 mm. Under ordinary pressure, it decomposes into hydrogen chloride and the hydrocarbon. When treated with alkalis, the hydrochloride yields the hydrocarbon, but there is no appreciable formation of any oxygen compound. All its properties agree with those of a menthol-derivative, and the hydrocarbon is identical or isomeric with Oppenheim's menthene. It is evident also that there is a close relation between terpilene and menthene. C. H. B.

Essential Oil of Daucus Carota. By M. LANDSBERG (*Chem. Centr.*, 1888, 1273).—By means of fractional distillation, this oil was divided into two principal fractions, the one boiling at 159—161° and the other at 240—260°. The former contains no oxygen, and is a terpene of the formula $C_{10}H_{16}$. It is dextrorotatory; a column 100 mm. long rotating the plane 32·3°; sp. gr. = 0·8525 at 28°. With bromine, it forms an additive compound, $C_{10}H_{16}Br_2$; from this, cymene was obtained by boiling its alcoholic solution with an aqueous solution of potassium cyanide. On heating the terpene in a closed tube at 280°, it is split up into two terpenes, the one boiling at 178—182°, and the other not distilling at 300°. Both combine with bromine to form additive compounds; that from the former, $C_{10}H_{16}Br_4$, melts at 123—125°; that from the latter has the formula $C_{10}H_{16}Br_2$. They may be considered as polymerides of the original terpene, which belongs to the group of pinenes.

The second component of the essential oil (boiling point 240—260°) proved to be a monohydrated terpene of the formula $C_{10}H_{18}O$. When heated to 280°, it loses the elements of water, and the residue consists of the same polymeric terpene of high boiling point as is obtained by heating the first-named terpene at 280°. The behaviour of the monohydrated terpene with bromine and with hydrogen chloride or bromide proved it to be identical with Wallach's cineole. J. W. L.

Constitution of Quassin. By V. OLIVERI (*Gazzetta*, 18, 169—170).—In a previous communication (Abstr., 1888, 1312), the author pointed out that quassic acid contained two ketonic groups, since it gave rise to a dioxime of the formula $C_{28}H_{36}O_8(C:NOH)_2$. It seemed, however, desirable to establish that these CO-groups existed also in quassin, and for this purpose the author prepared the compound of quassin with phenylhydrazine. Quassin (3 grams) and phenylhydrazine hydrochloride (4 grams) were dissolved in the smallest possible quantity of alcohol, a solution of sodium acetate added (6 grams in 15 c.c. water), and the whole heated at 100° for an hour. The yellow, amorphous deposit formed on allowing it to remain for a day was thoroughly washed with water, and attempts made to obtain it in a crystalline state but without success. An analysis showed that it had the composition $C_{30}H_{40}O_8(CH\cdot NHPh)_2$. It is formed from phenylhydrazine and quassin, with elimination of the elements of water, thus: $C_{30}H_{40}O_8(CO)_2 + 2NH_2\cdot NHPh = C_{30}H_{40}O_8(CN\cdot NHPh)_2 + 2H_2O$.
C. E. G.

Methysticin. By C. POMERANZ (*Monatsh.*, 9, 863—864).—Methysticin is a non-nitrogenous, non-volatile, neutral substance, which occurs in the alcoholic extracts from the roots of *Macropiper methysticum*. It crystallises in long, silky needles melting at 131°, sparingly soluble in hot water, ether, and light petroleum, readily soluble in alcohol, benzene, and chloroform. It contains about 65·4 per cent. carbon and 5·1 per cent. hydrogen. When fused with potash, it gives chiefly protocatechuic acid. Heated with 30 times the amount of 10 per cent. potash solution, it completely dissolves, and from the solution, which smells strongly of piperonal, hydrochloric acid precipitates a yellowish compound, which separates from alcohol in small white crystals melting at 180°. This compound, which contains 64·26 per cent. carbon and 4·85 per cent. hydrogen, is readily soluble in alkaline carbonates, and yields piperonylic acid on oxidation with permanganate. H. C.

Note.—No reference is made to Davidoff's researches on this subject (compare Abstr., 1888, 1207).

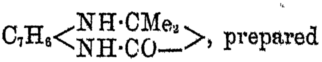
Andromedotoxin. By P. C. PLUGGE and H. G. DE ZAAYER (*Arch. Pharm.* [3], 26, 997—998, from *Arch. ges. Physiol.*, 40. See Abstr., 1883, 349).—Plugge first obtained andromedotoxin, which he extracted from *Andromeda japonica*, *A. polifolia*, *A. catesbaci*, and *A. calyculata*.

The aqueous extract of *Rhododendron ponticum* leaves was treated successively with normal and basic lead acetate. From the filtrate, the lead was separated by hydrogen sulphide, and the liquid was concentrated by slow evaporation in the air, and treated repeatedly with considerable quantities of chloroform. The residue left on evaporating the chloroform was purified by re-solution in chloroform (or alcohol) and precipitation by the addition of a considerable amount of ether. This treatment several times repeated finally yielded well formed, crystalline needles which melted at 228—229°. At 125°, water dissolves 2·81 per cent.; alcohol (of 94 per cent.) 11·1; amyl alcohol, 1·14; chloroform, 0·26; ether, 0·07; benzene, 0·004. The solutions in water, alcohol, and amyl alcohol are lævorotatory, whilst that in chloroform is dextrorotatory. Andromedotoxin, $C_{31}H_{51}O_{10}$, is an indifferent non-nitrogenous compound; its solution in indifferent liquids has a neutral reaction, and it is not precipitated by any of the so-called general alkaloïd reagents. Its reaction with dilute and concentrated mineral acids is characteristic, as with them it gives intensely red decomposition-products. Concentrated sulphuric acid gives a dark reddish-brown, which becomes deeper red on warming, and turns light mulberry-red on dilution with water. The addition of alkali removes the colour, which reappears on acidifying. Evaporation with dilute (1 : 5) sulphuric acid gives a beautiful rose-red colour. The pure material gives off no odour during this evaporation, but if not completely purified, a strong and very characteristic odour of ericinol is evolved. Evaporation with dilute hydrochloric acid gives a residue somewhat more violet-red in tint. Evaporation with phosphoric acid gives a mulberry-red residue, clearly perceptible with very minute quantities, as in the case of the other acids. The fatal dose for small animals has been found to vary from 0·1—0·45 mgrm. per kilo. body-weight. No chemical antidote is known as yet. In investigating poisoning cases, Dragendorff's process is recommended; but no acid should be used for extraction, as the solubility of the poison is not thereby increased. After extraction and purification by evaporation, taking up in alcohol, &c., the substance may be agitated with light petroleum, then with chloroform, and to the residue left by the chloroform the characteristic tests given above may be applied.

J. T.

Chlorophyll. By E. SCHUNCK (*Proc. Roy. Soc.*, **44**, 448—454; compare Abstr., 1887, 972).—Crude chlorophyll from grass is treated with boiling alcoholic soda, and hydrogen chloride passed into the solution until it is strongly acid. Crystals separate, which after purification form a semi-metallic purple mass, which softens at 205°, and shows the absorption-spectrum of phyllocyanin-derivatives. This compound is an ethyl ether. On treating it with boiling alcoholic soda, a dark-green sodium salt is obtained, which when decomposed by acetic acid and crystallised from ether gives purple crystals of a new substance, *phyllotaonin*, melting at 184°, and insoluble in water, but soluble in boiling alcohol and ether. The solution shows the same bands as phyllocyanin, but if the smallest quantity of acid be added, the third band from the end becomes fainter, and the fourth and fifth bands split into two. It forms a compound with acetic acid. Phyllotaonin forms compounds with potassium, sodium, copper, iron, and silver. With tin and hydrochloric acid, it gives a red compound, similar to that produced from phyllocyanin with the same reagents. A compound similar to the ether mentioned above may be obtained by treating phyllotaonin with ethyl iodide and potassium hydroxide; it is a black substance, whose solution gives an absorption-spectrum similar to that of the above ether. When chlorophyll is treated with alkalis and then with acids, it probably yields phyllotaonin, which in the nascent state, in contact with alcohol and hydrochloric acid, undergoes etherification. Crystallographic measurements of phyllotaonin are given. H. K. T.

Hydroxyhydroquinoxalines. By O. HINSBERG (*Annalen*, **248**, 71—84).—The author has repeated the experiments of Plöchl (Abstr., 1886, 351) and of Leuckart (*ibid.*) on the reduction of nitrotolylglycin by tin and hydrochloric acid, and finds that the product is identical with the dihydrohydroxytoluquinoxaline which is formed by the action of ethyl chloracetate on toluylenediamine. This substance rapidly oxidises, forming hydroxytoluquinoxaline, which Plöchl and Leuckart mistook for dihydrohydroxytoluquinoxaline. The substance described by Leuckart and Hermann (Abstr., 1887, 383) as chlorodihydrotoluquinoxaline, is also a derivative of hydroxytoluquinoxaline. Ethyl α-chloropropionate acts on toluylenediamine, forming an unstable compound, which oxidises on exposure to the air, yielding *hydroxymethyltoluquinoxaline*, $C_7H_6{<}\begin{matrix}N{:}C(OH)\\ N{:}CMe—\end{matrix}{>}$. The substance is crystalline, and melts at 238°. It is probably a mixture of two isomeric quinoxalines.

Dimethyloxydihydrotoluquinoxaline,  $C_7H_6{<}\begin{matrix}NH{\cdot}CMe_2\\ NH{\cdot}CO—\end{matrix}{>}$, prepared by the action of ethyl bromisobutyrate on toluylenediamine, is a stable crystalline compound, soluble in alcohol and ether. It melts at 227°, and yields a crystalline acetyl derivative, $C_{11}H_{13}N_2OAc$, melting at 206°. The *nitroso-derivative*, $C_{11}H_{13}N_2O{\cdot}NO$, melts at 153—154° with decomposition. The *dinitro*-compound melts at 280°. Dimethyloxydihydrotoluquinoxaline does not, like its apparent homologues, lose 2 atoms of hydrogen on oxidation, but undergoes a deeper change. Its whole behaviour shows that it does not belong to the class of hydroxyquinoxalines. W. C. W.

Metabromoquinolines. By A. CLAUS and G. N. VIS (*J. pr. Chem.* [2], **38**, 387—394).—The metabromoquinoline nitrate (m. p. 163°) previously obtained by Claus and Tornier (Abstr., 1888, 163), is really a mixture, and the oil obtained from it is not pure metabromoquinoline, as then described, but a mixture of both bromoquinolines, and generally contains some unaltered metabromaniline. When this nitrate is further fractionally crystallised, a nitrate melting at 185° (uncorr.) is obtained; the base separated from this crystallises in beautiful, colourless needles, melting at 48° (uncorr.), and as it has a higher melting point than the bromoquinoline previously described as anabromoquinoline (Abstr., 1888, 163), it is doubtless the real *anabromoquinoline*. Moreover this bromoquinoline can be obtained from ana-amidoquinoline by converting it into ananitroquinoline, and treating the latter by Sandemeyer's method.

The other bromoquinoline, previously described as anabromoquinoline (Abstr., 1888, 163), whose true melting point is 34°, is the real *metabromoquinoline;* its nitrate melts at 199°; its *methiodide* forms anhydrous yellow needles or prisms, melting at 240° (uncorr.).

When metabromoquinoline (1 part) is nitrated with a mixture (5 parts) of 2 parts of sulphuric acid and 1 part of nitric acid, two nitro-derivatives are obtained. *α-Nitrometabromoquinoline* crystallises in large, transparent prisms, which melt at 192° (uncorr.); its *platinochloride* is bright-red, and decomposes at 240°.

α Amidometabromoquinoline forms colourless needles which melt at 62° (uncorr.).

β-Nitrometabromoquinoline crystallises from alcohol in white aggregates of needles which melt at 142° (uncorr.), and has feeble basic properties; its *platinochloride* forms small, golden-yellow, anhydrous laminæ.

The *methiodide* of anabromoquinoline crystallises from hot water in yellow needles melting at 205° (uncorr.). Two nitro-derivatives are obtained by nitrating anabromoquinoline: *α-nitranabromoquinoline*, which crystallises in slender, nearly colourless needles, and melts at 146° (uncorr.), and *β-nitranabromoquinoline*, which also forms nearly colourless needles; it melts at 126° (uncorr.), and is a stronger base than the α-compound. The *platinochlorides* of both are described. A. G. B.

A Cerium Quinoline Nitrate. By G. WILLIAMS (*Chem. News*, **58**, 199—200).—When moderately concentrated solutions of ceric and quinoline nitrates are mixed, glistening, orange-red, rhombic plates of the double nitrate, $Ce(NO_3)_4,(C_9H_7N,HNO_3)_2$, form. The air-dried salt is amorphous, and melts readily, giving off nitrous fumes and an odour of nitrobenzene. On ignition it frequently deflagrates. D. A. L.

Additive Product of Papaverine with Orthonitrobenzyl Chloride. By E. v. SEUTTER (*Monatsh.*, **9**, 857—862).—20 grams of papaverine and 12 grams of orthonitrobenzyl chloride, finely powdered and mixed together, are heated for five hours on a water-bath. The product is extracted with water, excess of the chloride removed by agitation with ether, and the additive product obtained from the solution in light yellow crystals. These contain varying amounts of water according to the method used in drying them. The anhydrous product gives numbers for the chlorine and nitrogen which point to the composition $C_{20}H_{21}NO_4,C_7H_6NO_2Cl$. The nitrate, picrate and dichromate are described, as also the platinochloride. H. C.

Constitution of the Cinchona Alkaloïds. By Z. H. SKRAUP (*Monatsh.*, **9**, 783—827).—This paper contains the details of the investigation of the syrupy oxidation product of cinchonine and quinine (Abstr., 1887, 164). The syrup after removal of chromium by means of ammonia is treated with barium chloride and extracted with alcohol, and is thus separated into two portions, one, which is insoluble, containing the whole of the barium, and the other free from barium, which is soluble.

The barium salt of the organic acid present in the insoluble portion is converted into a lead salt, and this on analysis has the composition $(C_8H_{12}NO_4)_2Pb$. It is the salt of the monobasic acid $C_8H_{13}NO_4$ mentioned in the former paper, to which the name *cincholeuponic acid* is now given. By heating the lead salt with acetic anhydride at 120—130°, one of the hydrogen-atoms of this acid may be displaced by acetyl. Distilled with zinc-dust, a mixture of pyridine and its higher homologues is obtained, together with a large quantity of a non-volatile resin. The action of nitrous acid yields, among a variety of other products, a bibasic acid of the composition $C_8H_{12}N_2O_5$. On treatment with hydrogen chloride, this acid loses nitrous acid and becomes converted into the compound $C_8H_{13}NO_4,HCl$, a change which shows that the acid $C_8H_{12}N_2O_5$ is a nitroso- or isonitroso-derivative. On removing the hydrogen chloride from the above hydrochloride by means of silver oxide, cincholeuponic acid may be obtained in crystals. This acid, although monobasic, probably contains two carboxyl-groups, one of which only becomes active in the acetyl- and nitroso-derivatives.

That portion of the original syrup which is soluble in alcohol contains the three bases mentioned in the former paper. Of these the last, which is of doubtful origin and whose composition should have been given as $C_{13}H_{16}NO_2$, has been submitted to no further examination. The base $C_9H_{17}NO_2$, separated by means of its crystalline compound with gold chloride, is here named *cincholeupone*. It forms a crystalline compound with 1 mol. HCl; this has a slight optical rotatory power. When oxidised with chromic acid, cincholeuponic acid is obtained along with a number of basic substances. Heated with zinc-dust it gives β-ethylpyridine as the chief product, but no quinoline is formed. By means of acetic anhydride, one hydrogen-atom may be displaced by acetyl; the derivative thus obtained has the properties of a monobasic acid. By the action of alkyl iodides, 1 atom of hydrogen may be displaced by an alcohol radicle. The nitroso-derivative, $C_9H_{16}N_2O_3$, produced by the action of nitrous acid, has likewise the properties of a monobasic acid. The third base present, C_9H_7NO, which is separated by means of its platinochloride, is here identified with kynurine.

The author discusses the above results with reference to the constitution of cinchonine. He looks on cincholeupone as a secondary amine, being most likely a β-ethylpyridine-derivative, and considers it probable that cinchonine contains a quinoline-ring connected by at least two of its carbon-atoms with an ethylated pyridine-ring.

H. C.

Colchicine. By G. JOHANNY and S. ZEISEL (*Monatsh.*, 9, 865—881). —The view put forward by one of the authors (Abstr., 1888, 613) that colchicine is methylated colchiceïne, and this latter an acetyl-derivative of trimethylcolchicinic acid, is supported by synthetical evidence. By the action of methyl iodide on sodium colchiceïne, colchicine is produced, as also by passing hydrogen chloride through a solution of colchiceïne in methyl alcohol. In the first of these reactions a substance is also formed which appears to be *methylcolchicine*, $C_{22}H_{24}NMeO_6$; this, when boiled with dilute hydrogen chloride, yields methylcolchiceïne. Colchiceïne is produced by the action of acetic anhydride on trimethylcolchicinic acid.

Trimethylcolchicinic acid is found to crystallise with 2 mols. MeOH. When heated with sodium methoxide and methyl iodide in molecular proportions, a substance is obtained which the authors call *trimethylcolchidimethinic acid*, $COOH\cdot C_{15}H_9(OMe)_3\cdot NMe_2$, in which the hydrogen-atoms of the amido-group in the original acid have been substituted by methyl-groups. It melts at 126°. By the action of a further quantity of methyl iodide, the methiodide of the methyl salt of the above acid is obtained. This substance on treatment with silver oxide gives off trimethylamine, thus showing that it contains the NMe_3I group. H. C.

Action of Acid Chlorides on the Methyl Salt of Ecgonine Hydrochloride. By A. EINHORN and O. KLEIN (*Ber.*, **21**, 3335—3338).—The methyl salt of ecgonine hydrochloride, $C_8H_{14}NO\cdot COOMe,HCl + H_2O$, is obtained by saturating a solution of ecgonine hydrochloride in methyl alcohol with hydrogen chloride and heating the product in a reflux apparatus for an hour. It crystallises from alcohol in beautiful, transparent prisms and melts at 212° with decomposition.

The methyl salt of benzoylecgonine or cocaïne, $C_{17}H_{21}NO_4$, can be prepared by heating equal weights of the methyl salt of ecgonine hydrochloride and benzoic chloride at 100° for some hours until hydrogen chloride is no longer evolved. The base obtained by adding an alkali to the product has all the properties of the natural alkaloïd (compare Liebermann and Giesel, this vol., p. 168).

The methyl salt of *isovalerylecgonine*, $C_{15}H_{25}NO_4$, is formed by heating equal weights of the methyl salt of ecgonine hydrochloride and isovaleric chloride at 100° for 15 minutes. The base is an oil and could not be crystallised, although its hydrochloride, hydrobromide, and hydriodide crystallise well. The *platinochloride*, $(C_{15}H_{25}NO_4)_2,H_2PtCl_6$, forms large scales.

The methyl salt of *phenylacetylecgonine*, $C_{18}H_{23}NO_4$, is obtained by heating equal weights of the methyl salt of ecgonine hydrochloride and phenylacetic chloride at 100° for some hours. It is an oil which could not be crystallised, although its hydrobromide and hydriodide crystallise well from absolute alcohol. The *platinochloride*, $(C_{18}H_{23}NO_4)_2,H_2PtCl_6$, is crystalline.

The dimethyl salt of *orthophthalyldiecgonine*, $C_{28}H_{36}N_2O_8$, is prepared under like conditions from the methyl salt of ecgonine hydrochloride, and orthophthalic chloride. It is crystalline, and yields a hydriodide crystallising from alcohol in scales. The *platinochloride*, $C_{28}H_{36}N_2O_8,H_2PtCl_6$, crystallises in scales. W. P. W.

Cinnamylcocaïne. By C. LIEBERMANN (*Ber.*, **21**, 3372—3376).—*Cinnamylecgonine*, $C_9H_7O\cdot C_9H_{14}NO_3$, is prepared by heating a mixture of ecgonine (1 mol.) and half its weight of water with cinnamic anhydride (1 mol.) on a water-bath for an hour, grinding the product with 6—8 times its weight of water, filtering from unattacked cinnamic anhydride and from cinnamic acid, extracting the filtrate with ether to remove all cinnamic acid, and finally concentrating to the crystallising point. It crystallises in beautiful, vitreous, spear-like, anhydrous needles, melts at 216° with decomposition, is readily soluble in alcohol, and is precipitated from the alcoholic solution by ether. When boiled with hydrochloric acid, it is readily converted into cinnamic acid and ecgonine, and on treatment with dilute potassium permanganate solution it is at once oxidised, an odour of benzaldehyde being produced at the same time. The *aurochloride*, $C_9H_7O{\cdot}C_9H_{14}NO_3,HAuCl_4$, is anhydrous.

Cinnamylcocaïne, $C_9H_7O{\cdot}C_9H_{13}MeNO_3$, is obtained when a concentrated solution of cinnamylecgonine in methyl alcohol is treated with hydrogen chloride and allowed to remain in the cold for 24 hours in a closed vessel. It separates from a mixture of benzene and light petroleum in beautiful crystals with vitreous lustre, showing many faces, melts at 121°, and is insoluble in water, but soluble in alcohol, ether, acetone, chloroform, and benzene. The *hydrochloride* crystallises in colourless needles, and the *platinochloride*, $(C_{19}H_{23}NO_4)_2,H_2PtCl_6$, crystallises in microscopic needles melting at 217°. W. P. W.

Imperialine. By K. Fragner (*Ber.*, 21, 3284—3287).—*Imperialine*, $C_{35}H_{60}NO_4$, occurs in the bulbs of *Frittilaria imperialis*, and can be obtained in the pure state as follows:—The crushed bulbs are rubbed up with lime, the mixture dried at 100°, and extracted with hot chloroform. The extract is shaken with water acidified with tartaric acid, the alkaloïd precipitated from the concentrated aqueous solution with sodium carbonate, washed and recrystallised from alcohol. The yield is 0·08—0·12 per cent. It crystallises in short, colourless needles, turns yellow when heated at 240°, brown at 248°, and melts at 254°. It is very readily soluble in chloroform, moderately in hot alcohol, more sparingly in ether, benzene, light petroleum, and amyl alcohol, and very sparingly in water; the solutions have a bitter taste, and the specific rotatory power in chloroform solution is $[\alpha]_D = -35{\cdot}4°$. The *hydrochloride*, $C_{35}H_{60}NO_4,HCl$, separates from alcoholic hydrochloric acid in large crystals and is readily soluble in water and alcohol. A yellowish-red *platinochloride*, $(C_{35}H_{60}NO_4)_2,H_2PtCl_6$, and a yellow *aurochloride*, $C_{35}H_{60}NO_4,HAuCl_4$, are precipitated in oily drops when ether is added to an alcoholic solution of the hydrochloride and platinic or auric chloride; after having been washed with ether, both salts separate from hot dilute hydrochloric acid in a crystalline condition. The *sulphate* is very hygroscopic and was not obtained in a crystalline condition; the *oxalate* crystallises only from very concentrated solutions. Most of the usual reagents for alkaloïds produce precipitates in solutions of the salts. The free base turns pale yellow when treated with sulphuric acid, and when previously mixed with sugar it first becomes yellowish-green, then pale-green, flesh colour, cherry-red, and, after a long time, dark violet. Fröhde's reagent colours it greenish-yellow, and with Mandelin's reagent it gives an olive-green coloration which passes through reddish-brown and becomes dark brown. When mixed with potassium nitrate or potassium chlorate, and then moistened with sulphuric acid, it turns orange-yellow; if, however, the mixture is previously warmed, it turns dark reddish-yellow. The solution in hydrochloric acid fluoresces, becomes brownish-green when warmed, and turns brownish-red when the heating is continued for a long time. F. S. K.

Humous Substances. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **13**, 66—121).—On the death of plants or parts of plants, substances of a brown colour are formed which are called humous substances. Wood, however, often remains white for years. In dry air, or at a high temperature, plants can be dried without browning. The browning of the surface of a cut apple may be taken as a very rapid example of the process. Bacteria do not seem to be concerned in this change. This brown coloration does not occur to any extent in dead animal tissues. It is not, however, due to the chlorophyll of plants, as it occurs equally quickly in plants which contain no chlorophyll. The almost universal distribution of tannic acid and carbohydrates, and especially of cellulose, suggests that these may be sources of the humous substance, or it may come from the hydrocyanic acid, phenol, and nitrogenous compounds of plant tissues.

Pure cellulose when mixed with mud containing micro-organisms, ferments and yields carbonic anhydride and methane in the absence of oxygen, but no humous substance is formed (Abstr., 1886, 923); in the presence of oxygen, the cellulose (filter-paper) still remains quite white; all sorts of mud being used in the experiments. By heating with water at 188—200°, or with caustic alkalis, humous substances are formed. Water in glass tubes produced a brown residue, and the liquid was found to contain formic acid, catechol, and protocatechuic acid; when platinum tubes were employed, there was a brown residue, but the other products obtained in glass tubes were absent, as they are due to the decomposition of the humous substance produced by a small quantity of alkali, dissolved out from the glass at the high temperature to which the tubes were subjected. Other experiments were performed with strong alkalis, and the resulting gases, as well as the residue, were analysed.

The fermentation of wood-gum was found to be similar to that of cellulose; and it is supposed that the lignic acid may be instrumental in the formation of humous substances in turf, peat, &c.

Tannin red, obtained from certain plants by extracting with water, and the phlobaphen of Stähelin and Hofstetter, an amorphous brown substance, are apparently derivatives of tannic acid, and may be included under humous substances. The preparation and properties of a large number of these substances are described. They are formed by the action of alkalis on various carbohydrates (dextrose, lactose, cane-sugar, glycuronic acid, &c.); from various aromatic substances; and those obtained from various vegetable sources are also described. They are amorphous, differing in percentage composition, mostly containing nothing but carbon, hydrogen, and oxygen. A few contain nitrogen, like those described by Udránszky in urine (Abstr., 1887, 1133; 1888, 180). A derivative of humous substances called humic acid is described, and various names are given to various other members of the group.

The original paper must be consulted for details concerning their preparation and analysis; the following summary will, however, indicate the methods adopted in their separation.

Humous substances fall into three groups: the first includes those which are soluble neither in caustic alkalis nor in alcohol, but unite with alkalis, forming a slimy mass. This group includes the humin and ulmin of Mulder. The second group consists of those which are completely soluble in alkalis, and precipitable from such solutions by acids; the precipitate formed is voluminous and jelly-like, and is insoluble in alcohol. A part of the tannin reds, and of humic and ulmic acids, belong to this group. The substances in the third group resemble those in the second with regard to their solubility in alkalis; but the precipitate produced by acid is easily soluble in alcohol. Phlobaphen, a part of humic and ulmic acids, and the brown acids included under the name hymatomelanic acids (which are formed from the members of the first two groups by heating with caustic alkalis) belong to the third group. W. D. H.

Cholamide and Hippuramide. By G. Pellizzari (*Chem. Centr.*, 1888, 1350—1351, from *L'Orosi*, **11**, 233—235).—By heating glycocholic acid for one day at 160—170° with alcoholic ammonia under pressure, a residue was obtained on evaporating the liquid, which, when recrystallised from aqueous alcohol, appeared as long, silky, very deliquescent needles. These are insoluble in acids and alkalis, little soluble in boiling water, readily soluble in alcohol and ether, and melt about 125°. The composition corresponds with that of Hüfner's cholamide, $C_{23}H_{39}O_3 \cdot CONH_2$. Isoglycocholic acid reacted with ammonia in a similar way.

Hippuric acid, when heated with alcoholic ammonia for four hours at 210—220°, reacted with formation of hippuramide melting at 183°. By heating at 260°, a further change took place, ethyl benzoate and benzamide being formed. J. W. L.

Chinethonic Acid. By V. Lehmann (*Zeit. physiol. Chem.*, **13**, 181—186).—Phenetoïl leaves the body partly in union with glycuronic acid in the urine. After administration of this substance, an acid occurs in the urine called chinethonic acid (Kossel, Abstr., 1881, 631). It may be prepared as follows:—The urine is concentrated, acidified with sulphuric acid, and extracted with ethyl acetate; this is separated, treated with excess of barium carbonate and distilled off; the residue boiled with water, filtered hot, and the filtrate evaporated to a small bulk. In a few days, the barium double salt crystallises out; this is recrystallised, dissolved in hot water, and neutral potassium sulphate added as long as a precipitate of barium sulphate forms; this is filtered off, the filtrate evaporated to dryness, and the residue extracted with boiling alcohol; the potassium salt goes into solution, and on cooling, crystallises out; the potassium salts of the ethereal hydrogen sulphates remain in solution. Some of these latter are formed from the phenetoïl administered. The relation of total sulphuric anhydride to that combined as ethereal hydrogen sulphates was, in a dog, before the experiment = 8·92; after the administration of 12 grams of phenetoïl it fell to 2·74.

The potassium salt, $C_{14}H_{17}O_8K + H_2O$, of the new acid, occurs in monoclinic crystals, and the silver salt has the formula $C_{14}H_{17}O_8Ag + H_2O$. The free acid, $C_{14}H_{18}O_8$, obtained by treating the potassium salt with sulphuric acid, is crystalline, and melts at 146°. When treated with dilute sulphuric acid, an oily substance which subsequently crystallised was obtained; it had the formula $C_8H_{10}O_2$, that is, contained one atom of oxygen more than phenetoïl. The question arises whether the oxygen is united to the benzene nucleus, or is derived from oxidation of the ethyl-group. It was found that on decomposing chinethonic acid with hydrogen iodide, quinol is formed, and with oxidising agents, quinone is formed easily. The constitution of chinethonic acid is therefore $OEt\cdot C_6H_4\cdot C_6H_9O_7$. W. D. H.

Physiological Chemistry.

Digestion in Hydra. By M. GREENWOOD (*J. Physiol.*, 9, 317—344).—The paper includes many points of histological interest; those which relate to digestion are summarised thus:—(1.) The ingestion of solids is performed by slow advance over the prey of lip-like projections of the hydra's substance. Entomostraca, Nais, beetle larvæ, and raw meat prove the most acceptable food; innutritious matter does not act as a stimulus to digestion. (2.) The digestion of enclosed food takes place entirely outside the endoderm cells which line the enteric cavity, and among these may be distinguished: (*a*) pyriform cells destitute of large vacuoles, holding secretory spherules during hunger, and these empty during digestive activity; (*b*) ciliated vacuolate cells often pigmented: the water of the digestive fluid is probably derived from these vacuoles. (3.) The pigment occurs as brown or black grains; its basis is proteïd in nature. The pigment resists solution in most chemical reagents; it dissolves slowly in nitric acid. It may be expelled into the alimentary cavity during digestion. (4.) A reserve substance of proteïd nature accumulates during digestive acts in the basal part of the vacuolated cells, and eventually takes the form of spheres; the excretory pigment probably takes its rise in some residue from this absorbed proteïd; it is also possible that fat is similarly formed. (5.) The medium in which digestive activity goes on is probably not acid.

These observations relate to *Hydra fusca*. In *H. viridis*, which contains chlorophyll (the chloroplastids of Ray Lankester) the mode of nutrition seems to be different; gland cells do not form a conspicuous feature in its endoderm, and apparently digestive secretion is less active. W. D. H.

Influence of the Consumption of Water on the Alimentation of Animals. By W. HENNEBERG (*Bied. Centr.*, 1888, 813—818).—The author controverts the statements of Märcker and others who state that about 40 per cent. of the water consumed by animals reappears in the form of vapour. Making use of the statistics of several experiments, it is shown that the water which appears as urine and as dung forms, in sheep 61 to 92 per cent. of the whole water consumed, and in oxen, 83 to 93 per cent.; consequently Märcker's figure for vaporised water, namely, 40 per cent., is much too high; it should be for sheep on the average 25·8, for cattle 12·6. E. W. P.

Coagulation of the Blood. By L. C. Wooldridge (*Proc. Roy. Soc.*, **44**, 282—284).—An answer to criticisms by Halliburton (Abstr., 1888, 974).

Influence of Ethyl-alcohol on Metabolism in Man. By H. Keller (*Zeit. physiol. Chem.*, **13**, 128—134).—The experiment was carried out on the author's person, and lasted a week; the daily nourishment consisted of 500 grams of meat, 500 grams of bread, 100 grams of butter, 1500 c.c. of spring water, and 2 grams of common salt. On the 4th day, 150 c.c. of pure 96 per cent. ethyl-alcohol was mixed with the water.

The urine was carefully collected, and in it the chlorides, sulphates, phosphates, and total nitrogen were estimated. The following table gives the results obtained:—

Day.	Volume of urine.	Body-weight.	In the Urine.				Remarks.
			Cl.	P_2O_5.	SO_3.	N.	
	c.c.	gram.					
1	1746	62800	3·919	2·956	3·399	20·9	
2......	1317	—	1·848	3·280	3·255	22·0	
3......	1246	62250	1·459	3·288	3·311	22·2	
4.. ..	1720	62250	1·930	3·348	3·368	20·8	150 c.c. alcohol.
5......	880	61400	1·416	2·891	3·494	23·1	
6......	987	61850	1·200	2·696	3·323	23·1	
7......	1080	61905	1·441	3·112	3·458	23·1	

From this the following conclusions are drawn:—

1. Alcohol acts as a diuretic. This is what previous authors have observed (K. B. Lehmann, *Münchner med. Wochensch.*, 1886, No. 51, 1887, No. 23).

2. There is a slight lessening of the nitrogenous output on the day on which alcohol was taken. This is perhaps explicable from the destructive action of alcohol on digestive and absorption processes. The following days showed a slight increase of the total nitrogen in the urine.

3. The increase of phosphoric acid is too slight, and the length of the experiment too short to draw any certain conclusions concerning it.

4. The increase of chlorine is also very slight, and perhaps depends only on the diuretic action of the alcohol. W. D. H.

Metabolism of Acetanilide in the Human Body. By K. A. H. MÖRNER (*Zeit. physiol. Chem.*, **13**, 12—25).—The urine of patients taking this drug (antifebrin) was, as Müller first observed (*Deutsch. med. Wochensch.*, **13**, 27), red, from excess of urobilin. The amount of ethereal hydrogen sulphates in the urine is increased, and the urine reduces alkaline solutions of cupric oxide and is strongly lævorotatory. The urine was evaporated to a syrup, extracted with 90—93 per cent. alcohol; to the extract, half its volume of ether was added, and then a warm concentrated alcoholic solution of oxalic acid. The potassium ethyl oxalate and the ethereal hydrogen sulphate form a compound which can be crystallised and purified by recrystallisation. Three preparations were made and analysed, and the numbers obtained correspond with the formula $NHAc{\cdot}C_6H_4{\cdot}SO_4K,C_2O_4KEt$.

On taking antifebrin, then, a part of it is oxidised to form paracetamidophenol, and is excreted as an ethereal sulphate; whether other similar acids are formed it is not at present possible to say.

The strongly lævorotatory reducing substance is probably a derivative of glycuronic acid. W. D. H.

Metabolism of Furfuraldehyde in Fowls. By M. JAFFÉ and R. COHN (*Ber.*, **21**, 3461—3465).—When furfuraldehyde is given to dogs and rabbits, a glycocine compound of furfuracrylic acid is excreted in small quantity in the urine (Abstr., 1887, 1032). It is possible, however, that this compound is the chief transformation-product of furfuraldehyde, and that the greater part is further oxidised in the organism, a small proportion only escaping oxidation and appearing in the urine, since experiment shows that rabbits fed with furfuracrylic acid in quantities amounting to 6 grams, excrete barely 0·5 gram of the glycocine compound of the acid, and about 2 grams of pyromykuric acid, no less than 60—70 per cent. of the furfuracrylic acid undergoing decomposition in the organism.

Furfuraldehyde in aqueous solution was given to fowls, partially by the mouth and partially by subcutaneous injection, in quantities of 0·5—1 gram per day. The action was very marked, and resulted in death in the majority of cases after a few days. Pyromucic acid and pyromucornithuric acid were present in the excreta, but no trace of furfuracrylic acid or its derivatives could be detected.

Pyromucornithuric acid, $C_{15}H_{16}N_2O_6$, crystallises in very small, colourless needles or short, thin prisms, melts at 186°, carbonises when strongly heated with the evolution of a pungent odour resembling that of acraldehyde, and is sparingly soluble in ether, but readily soluble in alcohol, acetic acid and hot water. When heated with baryta-water, it hydrolyses quantitatively into pyromucic acid and ornithine (Abstr., 1878, 584). W. P. W.

Is the Benzene-nucleus destroyed in the Body? By N. JUVALTA (*Zeit. physiol. Chem.*, **13**, 26—31).—A dog was fed on meat mixed with a known weight of neutral sodium phthalate; before and after the experiment it was fed on bone, so that the fæces during the time of experiment could easily be distinguished from those before and after. The urine and the fæces were examined.

The fæces contained 29·55 per cent., and the urine 12·95 of the salt given; 57·5 per cent. was therefore unaccounted for; in a second experiment 68·76 per cent. was lost. There was no increase in ethereal hydrogen sulphates in the urine, and glycuronic acid compounds were also absent. Hence, not being able to account for the loss, the author concludes that the substance had been destroyed, and therefore that the benzene-nucleus can be destroyed by the animal body. W. D. H.

Chemical Examination of the Suprarenal Capsules. By F. Marinò-Zuco (*Gazzetta*, **18**, 199—207).—In 1883, Foa and Pallacani proved the poisonous nature of the extract of the suprarenal capsules, but did not succeed in isolating the compound which gave this property to the extract. The author commenced his researches by confirming this statement as to the poisonous nature of the extract, and found that a few c.c. of it was sufficient to cause death in a large rabbit when injected hypodermically. If, however, the solution was rendered slightly acid or alkaline, it no longer had any toxic power.

After various fruitless attempts to isolate the poisonous substance, the following method was adopted: Some 500 suprarenal capsules of the ox were ground up with about five times their bulk of water, and the mixture heated on the water-bath for some four to five hours. When cold, the liquid portion was expressed, and the residue again treated four times successively in the same manner. The extracts were united, and their proteïd matters precipitated by adding to the liquid its own volume of alcohol and half its volume of ether. After separating the precipitate, the alcohol and ether were removed by distillation, and acetate of lead added to the filtered solution. The abundant brown precipitate thus formed was removed, and the clear solution carefully precipitated with basic acetate of lead, which then threw down a dirty white precipitate consisting of lead chloride and organic lead salts. The clear solution, after treatment with magnesia or, better, with argentic oxide and filtration, gave precipitates with all the general reagents for alkaloïds, such as auric chloride, potassium mercuro-iodide, &c. The aurochloride was prepared and analysed, when it was found to have the composition of neurine aurochloride, $C_5H_{12}ON,HAuCl_4$, with which it agreed in physical properties and in yielding trimethylamine when decomposed. The platinochloride, $(C_5H_{12}ON)_2,H_2PtCl_6$, was also prepared and analysed.

The lead precipitate was next examined; after being well washed, it was suspended in water, decomposed by hydrogen sulphide, filtered, and the filtrate treated with baryta-water, which threw down a precipitate of barium phosphate. The excess of baryta was then removed from the solution by means of carbonic anhydride, and the clear liquid precipitated by basic acetate of lead, which threw down lead chloride mixed with lead salts of organic phosphatic acids. It was found to be impossible to separate these acids, but the presence of glycerophosphoric acid in the mixture was proved.

Now, although the presence of neurine in the suprarenal capsules will not of itself account for the powerfully toxic action of the extract, it was found that if the mixture of organic phosphatic acids mentioned above is saturated with neurine, a liquid is obtained which, even when very dilute, has all the poisonous properties of the extract itself. Experiments were also made with neurine orthophosphate and glycerophosphate prepared synthetically. It was found that the phosphate is far more poisonous than the hydrochloride; whilst the glycerophosphate is intensely poisonous, 0·1 of a milligram being sufficient to kill a frog.

The poisonous principle being a compound of neurine with an organic phosphatic acid, it is easy to understand how the action of acids or alkalis by destroying this combination renders the extract innocuous. C. E. G.

Sugar and Allantoïn in Ascitic Fluid. By R. Moscatelli (*Zeit. physiol. Chem.*, **13**, 201—204).—In a small number of cases of cirrhosis of the liver, sugar occurs in the urine (Cobrat, *Lyon. Méd.*, 1875, No. 15; Lépine, *Gaz. méd. de Paris*, 1876, 126; Quincke, *Berlin. klin. Wochensch.*, 1876, No. 38).

In the present case of liver cirrhosis, the urine was scanty, and gave no sugar reaction. The ascitic fluid, however, contained 0·15 per cent. of sugar. This was estimated by Fehling's method. Confirmatory tests, including the fermentation test, were also successful.

A crystalline substance was also separated in small quantities from the same pathological fluid, which chemically and crystallographically was identified as allantoïn. W. D. H.

Antiseptic Action of Bile Acids. By P. Limbourg (*Zeit. physiol. Chem.*, **13**, 196—201).—Bile and the bile acids have long been supposed to have an antiseptic action in the alimentary canal. The present research is directed to determining more accurately whether this is the case, by means of quantitative analysis.

Hirschler (Abstr., 1887, 310) has shown that phosphomolybdic acid precipitates some of the products of digestion (peptone, propeptone, &c.), while it does not precipitate certain others (amido-acids); these may be respectively termed Groups 1 and 2.

Artificial pancreatic juice was mixed with "Witte's peptone," and infected with bacteria from dog's fæces. Digestion was then allowed to take place, a solution of sodium cholate being added to a certain number of the specimens.

At the end of a certain interval, the following determinations were made:—(1) Total nitrogen; (2) nitrogen of substances belong to group 2; and (3) ammonia. The following tables (p. 292) give the results in percentages in two series of experiments.

The quantity of amido-acids and of ammonia in the specimens where the bile salt was present is thus smaller than in those where the salt was absent. In other words, these experiments performed outside the body fully confirm what one has been accustomed to believe occurs in the alimentary canal, namely, that bile prevents or hinders changes of a putrefactive nature there. W. D. H.

Time.	Nitrogen in Group 1.		Nitrogen in Group 2.		Nitrogen in Ammonia.	
	With addition of 1 per cent. sodium cholate.	Without.	With sodium cholate, 1 per cent.	Without.	With sodium cholate, 1 per cent.	Without.
Beginning of Expt. 1 ...	79·8		20·2		0	
After 24 hours	47·8	25·5	46·7	62·2	5·8	12·3
After 48 hours	33·7	0	55·6	70·5	10·7	33·9

	With addition of		With-out.	With addition of		With-out.	With addition of		With-out.
	0·5 per cent. sodium cholate.	0·25 per cent. sodium cholate.		0·5 per cent. sodium cholate.	0·25 per cent. sodium cholate.		0·5 per cent. sodium cholate.	0·25 per cent. sodium cholate.	
Beginning of Expt. 2 ...	59·3			40·7			0		
After 24 hours	50·7	44·6	32·9	49·1	55·1	66·0	0·16	0·26	1·10

Carbohydrates in Normal Urine. By N. Wedenski (*Zeit. physiol. Chem.*, **13**, 122—127).—Brücke, Bence-Jones, Pavy, Huizinga, Abeles, and others have affirmed the constant presence of small quantities of dextrose in normal urine; while others—Seegen, Külz, Moscatelli, &c., have denied it. The more recent work of Udránszky (Abstr., 1888, 180, 863) shows that carbohydrates are normally present in small quantities, and Landwehr (*Centr. Med. Wiss.*, 1885, 369) prepared animal gum from normal human urine.

In the present research, the urine was shaken with excess of benzoic chloride; insoluble benzoyl compounds of the carbohydrates are thus formed and crystallise out. Estimation of the carbon and hydrogen in these gave a result intermediate between those obtained by control experiments with glycogen on the one hand and dextrose on the other. This led to the conclusion that probably a mixture of two carbohydrates is present; this was confirmed by treatment with sodium hydroxide; part went into solution and the remainder was undissolved. The insoluble residue was soluble in alcohol and gave the tests for grape-sugar; the soluble part was found to consist of a substance having the reactions of animal gum. W. D. H.

Glycogen in Diabetic Urine. By W. Leube (*Chem. Centr.*, 1888, 1278—1279, from *Virchow's Archiv*, **113**, 392—393).—In the precipitate obtained by the addition of alcohol to the urine of healthy persons and of those suffering from diabetes insipidus, the author could not find any carbohydrate or glycogen; in the urine of persons suffering from diabetes mellitus, however, a carbohydrate in varying quantity was detected which proved to be glycogen. J. W. L.

Physiological Action of Paraxanthine. By G. Salomon (*Zeit. physiol. Chem.*, **13**, 187—195).—Recent researches on the physiological action of caffeïne and allied substances have suggested the necessity of working out the action of paraxanthine which is an isomeride of theobromine.

The experiments were made mostly on frogs; the lethal dose for these animals was found to be a weight equal to 0·15 to 0·2 per 1000 of body-weight when administered subcutaneously. Given by the mouth, larger doses are necessary to produce both physiological effects and death; this is even more the case when paraxanthine is given in the solid state—for the crystals are very insoluble. Like xanthine, theobromine, and caffeïne, this drug has an action both on the central nervous system and on the muscles; the action on the muscles occurs when the drug is applied locally to them. Their excitability is lessened, and ultimately disappears altogether. The muscles become hard, but complete rigor of the muscles during life is never seen. The action on the central nervous system is seen in abolition of reflexes.

The action of all these drugs is thus very similar; all produce the same creeping movements; then the disappearance of all spontaneous muscular activity and complete abolition of reflexes without a preliminary increase; the heart remains intact. Respiration is similarly affected by both theobromine and paraxanthine; it is first hurried, then slowed, and after death the lungs are found to be fully distended.

Caffeïne produces a rapid rigor of the muscles after death; this is not markedly the case with paraxanthine.

A few experiments on warm-blooded animals (mice) gave the following results: paresis of the hinder extremities and increase of reflex activity, producing tetanus; peculiar creeping, dragging movements are thus produced. The dose of the poison must be twice to four times as large as for frogs.
W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Constituents of Hedera Helix. By H. Block (*Arch. Pharm.* [3], **26**, 953—984).—The author confirms Davis' view that Posselt's hederic acid obtained from the fruit of the ivy is not an acid. Posselt's results were confirmed as to the presence of hederatannic acid, oleïc acid, and another acid, and glycerol. Cholesterin was also found in the fruit. From the leaves was obtained *hederaglucoside*, $C_{32}H_{52}O_{10} + 2H_2O$, which loses 1 mol. of water at 100°. Treatment with 4 per cent. sulphuric acid slowly causes decomposition, thus: $C_{32}H_{52}O_{10} + 2H_2O = C_6H_{12}O_6 + C_{26}H_4O_4 + 2H_2O$. The leaves also yielded carotin. An aqueous extract made from 20 grams of different parts of the plant was titrated with normal potash solution, the amount of alkali used was respectively for the root, 11·1 c.c.; stem, 14·2; small leaves, 18·6; middle-sized leaves, 17·6; large leaves, 17·8. The mineral constituents of 100 grams dried at 100° are given in the following table:—

	Root.	Stem.	Leaves.
K_2O	0·5333	0·6778	1·2381
Na_2O	0·0261	0·0234	0·2179
CaO	2·7100	1·5139	5·0432
MgO	0·1550	0·2902	0·3450
Fe_2O_3	0·0345	0·0681	0·0781
MnO	0·0059	0·0148	0·0074
Al_2O_3	0·0022	0·0031	0·0393
HCl	0·0364	0·0124	0·0819
SO_3	0·1214	0·1737	0·7115
P_2O_5	0·2192	0·2333	0·5841
CO_2	2·3527	1·6076	4·2384
Total	6·3400	4·9200	12·6000
Soluble in water	0·8557	1·2610	2·5080
Insoluble in water	5·4843	3·6590	10·0920

J. T.

Rare Constituents of the Ash of the Sugar-beet. By E. O. v. LIPPMANN (*Ber.*, **21**, 3492—3493).—The author has detected boric acid, vanadium, manganese, cæsium, and copper in minute quantities in the ash of the sugar-beet. The occurrence of boric acid and cæsium, either in the sugar-beet or in products derived from it, seems hitherto to have escaped notice. W. P. W.

Presence of Nitrites in Plants. By T. MODDERMAN (*Ann. Agronom.*, **14**, 423—424).—In the water exuding from the curved teeth on the leaves of a fuchsia plant, the author has detected nitrites by the following tests: potassium iodide, starch, and sulphuric acid; ferrous sulphate and sulphuric acid; sulphanilic acid and naphthylamine sulphate; diphenylamine and sulphuric acid; rosaniline in glacial acetic acid; and phenol and mercury nitrate. In the soil itself nitrites could only be detected by the extremely sensitive reaction with sulphanilic acid. J. M. H. M.

Occurrence of Boric Acid in the Vine and in Wine. By G. BAUMERT (*Ber.*, **21**, 3290—3292).—The author has examined German, French, and Spanish wines, and found that boric acid was present in every case; boric acid is also contained in the leaves, tendrils, &c., of the grape vine (compare Ripper, *Weinbau u. Weinhandel*, No. 36, 1888, and Solstein, *Pharm. Zeit.*, **33**, 312).
F. S. K.

Vegetable Fats. By H. JACOBSON (*Zeit. physiol. Chem.*, **13**, 32—65.)—The fats in peas, beans, vetch and lupinus seeds were investigated. The raw fats form thick, nearly black masses with a strong aromatic odour, and are easily soluble in ether, chloroform, carbon bisulphide, &c.

The fat was first saponified with 25 per cent. sodium hydroxide; the lead soap was also prepared; ether extracts of the two soaps were prepared, and also the fatty acids. There were, therefore, the following preparations to be investigated:—

(1.) The mother-liquor after saponifying with soda.
(2.) The ethereal extract from the sodium soap.
(3.) The ethereal extract from the lead soap.
(4.) The fixed fatty acids.

Fat from Beans.—The seeds contained 1·17 per cent. of fat. (1.) The mother-liquor from the soda soap contained the black pigment which was not further investigated, glycerol, and volatile fatty acids, especially valeric. A considerable quantity of chlorine, trimethylamine, and glycerophosphoric acid was also obtained; the last from decomposition of lecithin. The choline was identified by elementary analysis: its platinochloride was also prepared. (2.) The ethereal extract from the soda soap contains a substance like cholesterin. In elementary composition it agreed pretty well both with animal cholesterin and also with the paracholesterin prepared by Reinke and Rodewald (Abstr., 1881, 753) from *Aethalium septicum*, and the phytosterin prepared by Hesse (*Annalen*, **192**, 179) from peas. These compounds are probably isomeric. Its melting point is 131·5° to 132·5° (uncorr.); its specific rotatory power $[\alpha]_D = -31°$ to $-32°$, which is the same as that of phytosterin. The benzoic acid compound was prepared: it crystallises in thin, bright, rectangular plates, easily soluble in ether and chloroform, and melting at 145—145·5° (uncorr.). The acetyl-compound was also prepared. (3.) The ethereal extract of the lead soap contained the lead salts of oleic and erucaic acids. (4.) The fixed fatty acids separated by the fractional method consisted chiefly of palmitic acid, and an acid of the formula $C_{24}H_{48}O_2$ (see also Stürcke, *ibid.*, **223**, 307). Stearic acid was absent.

Fat from Vetches.—The seeds contained 3 per cent. of fat. (1.) The mother-liquor from the soda soap contained only small quantities of volatile fatty acids. Lecithin was also present. (2.) The ethereal extract of the soda soap contained a substance exactly similar to the cholesterin of bean fat. (4.) The fatty acids consisted of oleic and other acids, which were not further investigated.

Fat from Peas.—The seeds contained 1·79 per cent. of fat. (1.) The mother-liquor from the soap contained lethicin; volatile fatty acids were also present in greater quantities than in either beans or vetches. (2.) Cholesterin was prepared from the ethereal extract of the soda soap, as in previous cases; after removing it, a substance resembling ceryl alcohol in elementary composition, crystalline form and melting point was separated out. (3.) The fixed fatty acids consisted chiefly of palmitic acid. Stearic acid was absent, or only present in mere traces. Oleic acid composed 90 per cent. of the fatty acid obtained from the fat of peas.

Fat from Lupine Seeds.—The seeds contained 8 per cent. of fat. Volatile fatty acids (rather less abundant than in peas), lecithin, cholesterin, ceryl alcohol were present, as in pea fat. Of the fatty acids, oleic acid was by far the most abundant, then came palmitic acid, and then arachidic acid. Mere traces of stearic acid were present. W. D. H.

Gluten and its Presence in Wheat-grain. By W. JOHANNSEN (*Ann. Agronom.*, **14**, 420—423).—Against the hypothesis of a special ferment which, in the ordinary process of obtaining gluten from flour, converts certain globulins (vegetable myosin) into that substance, the author cites the following observations:—An artificial flour, made by mixing dried and pulverised gluten with pure starch, or by mixing moist gluten with starch, and drying and pulverising the mixture, yields a paste of gluten by the ordinary process, just like common flour, and, moreover, behaves in exactly the same way to heat, acids, and mercuric chloride, in respect of the quantity of gluten yielded. The injurious effect of mercuric chloride is immediate when strong solutions (1 per cent.) are employed; with weak solutions it is gradual, and increases with the length of time during which the mixture of flour and water is left at rest before washing on the sieve; and the quantity of gluten obtained when mercuric chloride is added is always greater with a fine sieve than with a coarser one. Hence the author believes this injurious influence to consist simply in a tanning or coagulating action on pre-existing particles of gluten. Using the microscope, the author finds that gluten does not exist in the grain in the position usually assigned to it, namely, the peripheral layers of endosperm cells, which really contain small and slightly resisting particles of nitrogenous matter, lodged in a soft protoplasmic mass rich in fatty globules. The alleged aleurone grains observed in these cells by Hartig, the author states to be fat globules disengaged by contact with water. The deeper and smaller cells, inside of the peripheral endosperm, are the ones containing the gluten, which is in a dry condition, inclosing grains of starch. Teasing in a drop of water sets these starch grains free, leaving the gluten in the form of viscous filaments. J. M. H. M.

Erythroxylon Coca grown in India. By C. J. H. WARDEN (*Chem. News*, **58**, 249—251, 260—262, 273—276).—Several samples of *Erythroxylon coca* leaves, grown in various districts in India, have been examined by the author; the mode of culture, altitude, and meteorological characters of the district, the kind of soil and manuring, and the methods of curing, being taken into consideration. The alkaloïd was estimated by Squibb's modified method:—the dry pulverised leaves were moistened with alcohol acidified with sulphuric acid, percolated with alcohol, the percolate mixed with acidified water, and extracted with ether, then rendered alkaline with sodium carbonate, and again extracted with ether. This extract was washed twice with water, dried and weighed; the amounts of "crude alkaloïd" so determined are given in the following table:—

District where grown.	Moisture.	Per cent. dry leaves.	
		Ash.	Crude alkaloïd.
Ranchi, young leaves	6·18	6·71	1·139
" mature leaves	8·22	8·99	0·883
Arcuttipore, Cachar	6·08	7·39	1·369
" "	6·72	6·36	1·671
Darjeeling	10·37	7·58	1·115
Alipore, Calcutta	10·42	10·23	0·358
Matelli	9·30	12·18	1·022
Chulsa, Dooars	5·71	7·62	0·610
Jaunpore	10·05	12·64	0·571

The crude alkaloïd was very faintly yellow, and in no case showed any tendency to crystallisation, although attempts were made to induce crystallisation by extracting at various temperatures, and without applying heat, and by employing different acids and solvents. The alkaloïd obtained is, nevertheless, quite similar to cocaïne from other sources in its physiological action, except that it seems to be more active. It dissolves readily in hydrochloric acid, and yields a soluble and insoluble platinochloride, the former containing 18·75, the latter 18·88 per cent. of platinum; discrepancies from the theoretical are assumed to be due to a variable quantity of cocamine (Hesse, Abstr., 1887, 1125) in the alkaloïd from Indian leaves. Both platinum salts yielded bases producing marked anæsthetic effects on the tongue; Howard has observed that the insoluble platinochloride obtained from other leaves was devoid of this property (Abstr., 1887, 1126). In one instance stellate crystals of the base from the soluble platinum salt were obtained. Applying Williams' method, the crude alkaloïd showed 2·89 per cent. of impurity, but the precipitates were not crystalline. It is noted that after the addition of ether to the acidified alcoholic solution, larger deposits of the sulphur-yellow cocatannic acid were obtained from those samples containing the highest percentages of alkaloïds, it is hence suggested that possibly cocaïne exists in the leaves as cocatannate.

Methods of cultivating the plants are described: the leaves are first gathered 1½ years after transplanting, subsequently, whenever they are sufficiently mature; and, although the method of curing does not appear to affect the quality or quantity of the alkaloïd obtained, nevertheless it is best, taking into consideration Paul's experience, to dry them, soon after gathering, at as low a temperature as possible, and when dry and cold to pack them closely in air-tight chests, as they are very hygroscopic. The quantity of alkaloïd produced increases with the age of the plants (which attain a height of from 2 to 6 feet) up to 10 years, and after 20 years a slight falling off is observed, although they are in their prime even when 35 or 40 years old.

From the above results, obtained from plants and leaves of various ages, it would seem that, in India, neither altitude nor rainfall have much influence on the proportion of alkaloïd in the leaves. The ash, in all cases except one, was white, the exception being an ash of a reddish hue from mature Ranchi leaves. A partial examination of some of the ash showed that they contained the following percentages:—

Samples from	Soluble constituents.	K cal. as KHO.
Darjeeling	44·42	29·26
Alipore, Calcutta	34·60	19·13
Arcuttipore, Cachar	59·02	29·84
Matelli	64·17	31·36

So that both nitrogenous and potash manures will probably be required in the future to keep up the yield from the same plantation.

D. A. L.

Volatile Alkaloïd in Pepper. By W. Johnstone (*Chem. News*, **58**, 235).—A volatile alkaloïd, seemingly from the analytical data piperidine, has been observed by the author in pepper, and chiefly in the husks. Nine samples of black pepper contained a maximum of 0·77, a minimum of 0·39, and a mean of 0·56 per cent. Long pepper 0·84, pepper refuse 0·74, three samples of white pepper 0·34, 0·21, 0·42 respectively, whilst the corresponding black pepper gave a maximum of 13·03, a minimum of 5·21, and a mean of 8·25 per cent.

D. A. L.

Composition of Rain-water. By A. Lévy (*Bied. Centr.*, 1888, 793—795).—The results of a second set of 11 years' examination of rain-water for nitrogen are here given, and the quantities obtained during the warm and cold seasons of the year are kept separate. The average during the several months of 10 years are as follows:—

Ammoniacal Nitrogen per Square Metre.

January..	82·3 milligrams.	July	72·1 milligrams.
February .	59·6 „	August ..	102·7 „
March ...	66·3 „	September	93·3 „
April	95·3 „	October..	88·3 „
May	70·7 „	November	83·5 „
June.....	95·4 „	December	91·5 „

making a total of 1001·0 mgrm. per square metre per annum, or 10·01 kilos. per hectare.

As to the nitric acid nitrogen, the average was 3·85 kilos. per hectare. Dew, fog, and snow-water are richer in ammonia than rain, whilst they are poorer in nitric acid. E. W. P.

Salt in Rain-water. By G. Bellucci (*Bied. Centr.*, 1888, 795).—At Perugia, 120 kilom. from the sea, and at a level of 412 metres above it, there was found in the rain-water during the months of March to December, 1886, an amount of sodium chloride equal to 3·734 kilos. per hectare per month, and during the whole of the year 1887 there was carried down a total of 42·531 kilos., or 3·544 kilos. per month per hectare; taking the rainfall for the two periods into account there was found 5 mgrms. per litre. As in England so in Italy, the rain of the winter months contains more salt than that of the summer. E. W. P.

American Red Clover. By F. Nobbe (*Bied. Centr.*, 1888, 821—826).—The yield and hardiness of American red clover are compared with that of European clovers, with the following results:—American clover stands considerably behind Holstein, Silesian, or Saxon seed. The heaviest crop was obtained from Holstein seed, whilst the lightest was from Steiermark. Cow-grass proves to be a plant of feeble power, for in the second year of its growth, the crop was very small and innutritious. The presence of rye-grasses reduces the yield of clover, so that it is unadvisable to mix clover seeds with more than 6—8 kilos. of grass seeds per hectare. E. W. P.

Value of Basic Slag as a Manure, as compared with Soluble Phosphate and Bone-meal. By E. Heiden (*Bied. Centr.*, 1888, 798—800).—The crop was a mixture of vetches and oats (2 : 1) manured with superphosphate, basic slag, and boiled-bone meal, all assisted by nitre. The results were unsatisfactory, and from them no definite conclusion can be drawn save that basic slag was not in this case the best manure. E. W. P.

Manuring Experiments on Heavy Soil. By E. HEIDEN (*Bied. Centr.*, 1888, 809—812).—In a former communication, an account was given of the experiments in which for 10 years plots had been manured respectively with the same manure; in 1885 they were all manured with farmyard manure, yet the yields were not equal, but in 1886 nitrogen and soluble phosphates were added, and then the results were equal; finally peas were sown in 1887, and manured with phosphoric acid and potash, with the result that the plot previously manured with lime brought the highest crop, next followed superphosphate, the lowest yield being off the ammonium sulphate plot. These crops show how necessary the presence of lime is for leguminosæ, especially on soils poor in that substance; they also show that for this purpose the addition of lime as lime is preferable to its addition as phosphate. E. W. P.

Influence of the Concentration of the Cream in Butter-making. By J. SEBELIEN (*Landw. Versuchs-Stat.*, 35, 321—335).—To examine a statement of Kirchner's (*Milchzeitung*, 1887, 733), the author made a series of experiments in which cream was taken and divided into two portions, from one of which butter was made after the addition of half, or once or twice its weight of skim-milk, and from the other portion without any addition. In some of the experiments, the cream was soured before churning; in others it was churned sweet. With a few exceptions, the experiments pointed to the following conclusions. Both with sweet and sour cream, the percentage of fat in the butter-milk was smaller when the cream was diluted than when it was unmixed, the difference being greatest when it was churned sweet; but on calculating the absolute amount of fat left in the butter-milk coming from equal amounts of cream, it was found that more fat was left in the butter-milk when the cream had been diluted, and the differences were again greatest in the case of the sweet cream. The time taken in churning was longest when the cream had been diluted. The dilution appeared not to affect the composition of the butter. H. H. R.

Analytical Chemistry.

Apparatus for Estimating the Amount of Gas Disappearing in a Reaction. By C. F. CROSS and E. J. BEVAN (*Chem. News*, 58, 215).—The authors describe an apparatus suitable for the determination of the volume of a gas disappearing in combination. It consists of a bottle fitted with a well-paraffined india-rubber stopper, through which two tubes pass, the one of narrow bore, bent at right angles, and fitted with a stopcock; the other of wide bore, terminating within the bottle in a large thin bulb, and carrying a piece of india-rubber tubing at the other end. In experimenting with lignocellulose, for example, the bulb is filled with the fibre, and a glass rod is thrust through the piece of india-rubber tubing, so as to press on the fibre; the bottle is filled with chlorine, the stopper inserted, and the bent tube, with the stopcock closed, connected with a gas apparatus having a suitable intervening stopcock for adjusting levels, which is done, with both stopcocks open, as soon as the temperature is right; the stopcocks are then closed, the bulb broken by means of the rod, the bent tube stopcock opened, the rising column of mercury then indicates the progress of the reaction, which is vigorous and well defined with lignocelluloses. A tube filled with fibre is placed between the bent tube and gas apparatus to intercept any chlorine, though none has been observed to diffuse. D. A. L.

Graduation of Tubes for Gasometric Purposes. By BERTHELOT (*Ann. Chim. Phys.* [6], **14**, 279—286).—The author recommends the following method for graduating very exactly, or for verifying the graduation of tubes throughout their length. The tube placed vertically is filled with pure mercury so that the level of the metal is slightly above the orifice of the tube, care being taken to expel all air-bubbles. A moderately thick piece of perfectly flat glass is then pressed over the mouth of the tube, the whole inverted and weighed to within about 1 cgrm. A corner of the glass plate is then slightly separated from the tube so that a small quantity of mercury escapes. After replacing the plate, the whole is placed on a horizontal surface and the graduation corresponding to the horizontal tangent at the surface of the meniscus carefully noted by means of a magnifying glass or small telescope. The loss in weight is then ascertained by weighing the tube as before or by weighing the mercury which has escaped, and this value, divided by the density of mercury at the temperature of the experiment, gives the exact volume of the tube shown by the graduation in question. 8 to 10 such operations can be made successively with the same tube in one hour.

F. S. K.

A New Form of Eudiometer. By W. MARCET (*Proc. Roy. Soc.*, **44**, 383—387).—A eudiometer tube, open at the lower end, plunges into mercury; at the upper end is a steel cap fitted with a three-way stopcock which allows the eudiometer and tubes to be washed, either with pure hydrogen from a gasholder or with the air to be analysed. Hydrogen is first introduced, and then air. Results obtained with this apparatus are given. H. K. T.

Calorimetric Bomb as a Combustion Furnace for Ultimate Analysis. By A. EILOART (*Chem. News*, **58**, 284).—The author suggests the possible adoption of the calorimetric bomb, filled with an atmosphere of dry oxygen under pressure, for quantitative combustion, small absorption vessels for estimating the water and carbonic acid formed being introduced inside the bomb. A bomb much smaller than that used for calorimetric purposes would do. D. A. L.

Estimation of Hydrogen Peroxide. By C. T. KINGZETT (*Analyst*, **13**, 62—63).—The author has shown (Trans., 1880, 803) that hydrogen peroxide can be determined by adding a sufficiency of potassium iodide and sulphuric acid and titrating the liberated iodine with thiosulphate. To titrate 10 c.c. of a 2-volume solution (to which strength stronger solutions should be diluted) there is required 20 c.c. of a 10 per cent, solution of potassium iodide and 20 c.c. of dilute sulphuric acid (1 to 5). If a stronger potassium iodide solution (10 c.c. of 20 per cent.) is used, half that quantity of acid is enough. With smaller quantities, either of iodide or of acid, less thiosulphate was consumed, and the colour returned on standing. M. J. S.

Estimation of Chlorine. By G. LINOSSIER and M. LIGNON (*Bull. Soc. Chim.*, **50**, 354—355).—The cold or slightly warm solution of the chloride is precipitated with mercury nitrate; the analysis is carried out in a manner similar to the other acids (this vol., pp. 75 and 308). Poirrier's orange is used as indicator. The method may be used in determining chlorine in urine. N. H. M.

Volumetric Estimation of Chlorine. By J. T. WHITE (*Chem. News*, **58**, 229—230).—About 45 c.c. of a solution containing chlorides is mixed with 1 gram of permanganate and 5 c.c. of sulphuric acid diluted with an equal volume of water; this is then gently heated in a current of carbonic anhydride free from acid, the liberated chlorine absorbed in a solution of potassium iodide, and the free iodine titrated with thiosulphate; the results obtained are good. If bromine and iodine are also present in the solution, the former is first separated by boiling with permanganate and aluminium sulphate (free from or containing a known quantity of chlorine); the chlorine may then be estimated in the above manner, and the iodine remains behind as iodate.

The iodine of an iodide may be distilled from mixtures containing chlorides and bromides by ferric chloride, chromic acid, and hydrogen peroxide. D. A. L.

A New Method of Estimating Free Hydrochloric Acid in the Contents of the Stomach. By J. SJÖQVIST (*Zeit. physiol. Chem.*, **13**, 1—11).—The oldest method is that of Bidder and Schmidt, who were the first to prove the existence of free hydrochloric acid in the gastric juice. Rabuteau's method, modified by Cahn and v. Mering (*Deut. Arch. klin. Med.*, **39**, 239), consists in distilling off the volatile acids and shaking the residue with a large excess of ether which takes up the lactic acid; this is separated, and cinchonine is added to the remainder until the reaction is neutral, then it is shaken four or five times with a large excess of chloroform, which takes up the cinchonine hydrochloride; the chloroform is distilled off, and the chlorine estimated in the residue. Another method devised by Cahn and v. Mering consists in distilling the contents of the stomach with water three times. The volatile fatty acids are estimated in the distillate. The residue is shaken six times with 500 c.c. of ether, and this is evaporated to dryness, and the lactic acid estimated by titration. The residue contains the hydrochloric acid, and this also can be estimated by titration.

Another method used by Seemann (*Zeit. klin. Med.*, **5**), and Hehner (*Zeit. anal. Chem.*, **17**, 236), consists in neutralising the stomach-contents by titrating with sodium hydroxide, evaporating to dryness, and carefully incinerating. The ash is extracted with water, and in the extract the alkali present is estimated by titrating with an acid; the difference between the amount of alkali added, and the amount of alkali found, gives the amount which must have combined with hydrochloric acid.

This method, however, gives too high results; and the other methods take too long, and too large a quantity of the necessary reagents to be available for clinical work.

The method now recommended gives absolutely accurate results, and is sufficiently simple to use clinically. The contents of the stomach are evaporated to dryness with barium carbonate and then incinerated; barium chloride remains unchanged, and the salts of the organic acids are burnt to barium carbonate. The barium chloride is then extracted with water, and the quantity of barium dissolved is a measure of the original amount of free hydrochloric acid. The barium may be estimated by Mohr's titration method. In this method, potassium dichromate is added to the barium solution, by which means a precipitate insoluble in water and acetic acid is formed; the indicator of the end of the reaction is the yellow colour which the smallest excess of the dichromate gives to the liquid which floats over the precipitate. A more delicate test for excess of the dichromate is, however, Wurster's tetramethylparaphenylenediamine paper. Potassium dichromate in an acetic acid solution acts in the same way as ozone, to test for which the paper was originally used; it turns it blue.

The titration is carried out as follows:—The solution of barium chloride is placed in a beaker, and a quarter of its volume of alcohol added, then a few c.c. of a 10 per cent. solution of sodium carbonate containing 10 per cent. of acetic acid. A standard solution of potassium dichromate is then added from a burette till the end-reaction is obtained. Directions are given for the preparation of the standard solution: the most convenient was found to be one of which each c.c. corresponded to 4·05 mgrms. of HCl.

The method was tested with known strengths of hydrochloric acid, and mixtures of hydrochloric and lactic acids, and with artificial gastric juice. The results obtained were exceedingly accurate. The paper concludes with the account of the results obtained from actual stomach-contents by the use of the method. These may be summarised as follows:—

Case.	Reactions for HCl.	Reactions for lactic acid.	Percentages.	
			Total acidity.	HCl.
1	Doubtful	Well marked	0·15	0·02
2	Positive	Positive	0·29	0·132
3	„	„	—	0·076
4	„	Doubtful	0·2	0·138
5	„	Positive	0·295	0·144
6	„	Weak	0·189	0·164
7	Negative	Positive	0·14	0·03

W. D. H.

Separation and Estimation of Chlorine, Bromine, Iodine, and Cyanogen. By G. Errera (*Gazzetta*, 18, 244—258).—Although it is but seldom in ordinary analytical work that cyanogen has to be determined in the presence of chlorine, bromine, and iodine, yet it frequently happens in determinations of the halogens in organic compounds by combustion with lime, that cyanogen is formed, and is precipitated along with haloïd silver salts. The method adopted by the author is founded on the successive action of the halogen acids on the mixed silver salts.

1. *Separation of Cyanogen from one of the three Halogens and of two Halogens from one another.*—In determining cyanogen and chlorine, the mixed silver salts, dried at 100° and weighed, may be treated with hydrochloric acid, but the action is slow; the increase in the weight of the precipitate multiplied by 14·23216 gives the weight of the silver cyanide present which has been decomposed, and the chloride originally present can be estimated by difference. It is, however, far better to treat the mixed salts with hydrobromic or hydriodic acids. In this case, both the cyanide and chloride are converted into silver bromide or iodide, as the case may be. The formulæ for the calculation are—

$$x = \frac{an + b(n + 1)}{n - m}, \qquad y = \frac{am - b(m + 1)}{m - n}.$$

where y is the cyanogen, x the chlorine, a the weight of the mixed silver cyanide and chloride, b that of the silver in these mixed salts (calculated from the weight of the final product, silver bromide or iodide), n the ratio of silver to cyanogen in silver cyanide, m the ratio of silver to chlorine in silver chloride. The same formulæ are applicable to the other halogens.

In estimating two halogens in the presence of one another, the ordinary process of treating the mixture with gaseous chlorine is the best.

2. *Separation of Cyanogen from two of the Halogens and of the three Halogens from one another.*—The mixture of silver cyanide with the silver halogen compounds is carefully dried at 100° and treated with fuming hydrochloric acid, this converts the silver cyanide into chloride, but leaves the other silver salts unacted on; the product is then

dried at 100°, heated until it fuses and weighed. It is then heated in a current of chlorine and again weighed.

Let x and y be the amount of the halogens, and v that of the cyanogen. Also a the weight of the original precipitate of mixed salts, c the weight after treatment with hydrochloric acid (or hydrobromic acid), and b the total weight of silver present, calculated from the silver chloride obtained as the final product.

The equations are as follows for the three mixtures:—

$$\begin{aligned}\mathrm{Cy} &= v = (c - a)\,2{\cdot}76679.\\ \mathrm{Br} &= y = c\,1{\cdot}79680 - b\,2{\cdot}38711.\\ \mathrm{Cl} &= x = a\,3{\cdot}76679 + b\,1{\cdot}38711 - c\,4{\cdot}56361.\end{aligned}$$

$$\begin{aligned}\mathrm{Cy} &= v = (c - a)\,2{\cdot}76679.\\ \mathrm{I} &= y = c\,1{\cdot}38796 - b\,1{\cdot}84395.\\ \mathrm{Cl} &= x = a\,3{\cdot}76679 + b\,0{\cdot}84395 - c\,4{\cdot}15476.\end{aligned}$$

In the case of a mixture of cyanide, bromide, and iodide it is better to treat with hydrobromic acid instead of hydrochloric acid. In this case the equations are—

$$\begin{aligned}\mathrm{Cy} &= v = (c - a)\,0{\cdot}48308.\\ \mathrm{I} &= y = c\,2{\cdot}70501 - b\,4{\cdot}70902.\\ \mathrm{Br} &= x = a\,1{\cdot}48308 + b\,3{\cdot}70902 - c\,3{\cdot}18810.\end{aligned}$$

With a mixture of the three halogens, the weighed silver precipitate is treated with hydrobromic acid, weighed, and then heated in a current of chlorine as above.

$$\begin{aligned}\mathrm{Cl} &= v = (c - a)\,0{\cdot}79680.\\ \mathrm{I} &= y = c\,2{\cdot}70501 - b\,4{\cdot}70902.\\ \mathrm{Br} &= x = a\,1{\cdot}79680 + b\,3{\cdot}70902 - c\,3{\cdot}50180.\end{aligned}$$

3. *Separation of Cyanogen from the Halogens when all three of the latter are present.*—The precipitate of mixed silver salts is dried at 100°, divided into two portions and weighed. One of these is treated with fuming hydrochloric acid, avoiding as far as possible any great excess of the acid, dried at 100°, heated until it fuses, and weighed. The second portion is treated with hydrobromic acid of sp. gr. 1·49 in precisely the same way, and the product after fusion and weighing is heated in a current of chlorine and again weighed. If x, y, z, and v be the quantities of chlorine, bromine, iodine, and cyanogen present, a the weight of the mixed silver salts, c the weight of these (calculated) after treatment with hydrochloric acid, d the same after treatment with hydrobromic acid, and b the total weight of silver present calculated from the silver chloride obtained as the final product, then

$$\begin{aligned}\mathrm{Cy} &= v = (c - a)\,2{\cdot}76679.\\ \mathrm{I} &= z = d\,2{\cdot}70501 - d\,4{\cdot}70902.\\ \mathrm{Br} &= y = b\,3{\cdot}70902 + c\,1{\cdot}79680 - d\,3{\cdot}50180.\\ \mathrm{Cl} &= x = (d - c)\,0{\cdot}79680 - (c - a)\,3{\cdot}76679.\end{aligned}$$

In the paper, full details are given of the way in which these equations are obtained, and also results obtained by the use of the methods described. C. E. G.

Estimation of Sulphur in Burnt Pyrites. By J. Watson (*J. Soc. Chem. Ind.*, 7, 305—307).—The following volumetric method for the estimation of total sulphur has been in daily use at the Newcastle Chemical Works for about nine years, and during that time has been introduced into other works where it appears to have displaced Pelouze's gravimetric method. 2 grams of sodium hydrogen carbonate of known alkalinity is mixed in a platinum crucible with 5·16 grams of the powdered sample of burnt ore, and heated gently over a low Bunsen flame for about five minutes, after which the mass is broken up with the end of a wire stirrer. The heating is then increased and continued for 10 or 15 minutes, when the mass is washed out with warm water into a beaker, boiled for 15 minutes, filtered, and washed. The filtrate is then titrated with standard hydrochloric acid, using methyl-orange as indicator.

The author has found this method useful also in ascertaining what proportion of the residual sulphur in burnt ore exists as sulphide, which should have been available for acid making with perfect combustion. He proposes to estimate the soluble sulphur and deduct this from the total sulphur found by the volumetric method just described, the difference being the sulphur existing as sulphide.

A convenient method of estimating the soluble sulphur is by boiling a weighed quantity of burnt ore with a known quantity of standard sodium carbonate, filtering, washing, and titrating the filtrate with standard acid. For green ore, the method is not satisfactory, although various modifications have been tried by the author. D. B.

Volumetric Estimation of Acids. By Engel (*Bull. Soc. Chim.*, 50, 197).—A claim to priority as regards the method for sulphuric acid described by Linossier (this vol., p. 75).

Volumetric Estimation of Sulphates. By D. Sidersky (*Chem. Centr.*, 1888, 1293, from *Mon. Sci.*, 32, 1132—1139).—The method depends on the double decomposition between sodium carbonate and barium chloride. To the solution containing sulphates, an excess of barium chloride is added, and this excess is determined by the addition of sodium carbonate until phenolphthaleïn shows the presence of the latter in excess, or the reaction becomes sharper still if, instead of titrating the excess of barium chloride with sodium carbonate, a quantity of sodium carbonate equivalent to the added barium chloride is added, and then the excess of the sodium carbonate titrated with barium chloride in the presence of phenolphthaleïn.

The solution must be perfectly neutral, and any sulphides, thiosulphates, or sulphites present must be removed. So also the presence of calcium or magnesium oxide and of phosphoric or oxalic acids must be avoided. J. W. L.

The true Rôle of Soda-lime in the Estimation of Nitrogen. By Quantin (*Bull. Soc. Chim.*, 50, 198—201).—The usual explanation of the action of the soda-lime in nitrogen determinations is that the water of the alkaline hydroxide being decomposed by the carbon of the organic substance, yields nascent hydrogen which combines with the nitrogen to form ammonia. Experiments were made in which calcined sand, calcium carbonate and sulphate, baryta, and lime were used instead of soda-lime; the nitrogen is still given off as ammonia, but there remained a carbonaceous residue containing nitrogen. The author considers that the action of the soda-lime is to convert this residue of nitrogen and carbon into sodium cyanide, and that this is transformed by water-vapour from the back part of the tube into sodium carbonate and ammonia; further, that a very high temperature is unnecessary. These views are supported by the results of experiments which are described. N. H. M.

New Method for the Estimation of Nitrogen. By J. H. SMITH (*J. Soc. Chem. Ind.*, **7**, 307—308).—The method, which is a modification of the process of estimating organic substances by oxidation with potassium permanganate (Abstr., 1888, 90), consists in attacking the nitrogenous product with a large excess of potassium permanganate and a small amount of potassium bromide—bromine being alternately liberated by the permanganate and reduced to hydrobromic acid whilst oxidising the organic substance and liberating or further oxidising its nitrogen, a small amount of bromide thus serving to oxidise a comparatively large amount of organic substance.

The author gives the results of experiments on the oxidation of ammonia, cyanides, and carbamide in acid bromide permanganate solution, which show, in the case of ammonia, an oxidation of 72 per cent. of the total nitrogen to nitric acid, with cyanides complete oxidation to carbonic anhydride and nitric acid, and with carbamide first oxidation, as in the well-known alkaline hypobromite reaction, and subsequently oxidation of the nitrogen as in the case of ammonia.

The investigation is being pursued with the view of ascertaining whether this oxidation of nitrogen is likely to vitiate determinations of organic matter by permanganate. D. B.

Estimation of Phosphoric Acid with Silver Nitrate. By J. CLARK (*J. Soc. Chem. Ind.*, **7**, 311—312).—The author has investigated the accuracy of Perrot's volumetric process for the estimation of phosphoric acid based on precipitation as silver phosphate (Abstr., 1882, 94). His experiments show that with pure materials the method is capable of yielding good results in the absence of iron and alumina; but when applied to manures and natural phosphates the following modifications are necessary:—(1.) The dissolution of the silver phosphate precipitate in nitric acid and titration of the silver with thiocyanate. (2.) The neutralisation of the acid solution with aqueous soda instead of ammonia to avoid the presence of an excessive quantity of ammoniacal salts which affects the results. (3.) The previous precipitation of the iron and alumina as phosphate by means of sodium acetate containing free acetic acid. D. B.

Estimation of Nitrogen in Vegetable Soils. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **107**, 852—854).—Vegetable soil carefully freed from occluded air by repeated treatment with carbonic anhydride, was enclosed in a well-stoppered flask filled with carbonic anhydride. Under these conditions, there can be no alteration in the total quantity of nitrogen present. The total nitrogen was determined before the soil was put into the flasks in May, 1888, and again in October, 1888. Three different varieties of soil were analysed, and the numbers represent the amount of nitrogen per kilo. of soil dried at 110°.

	May.		October.	
Kitchen garden	0·974	gram.	0·986	gram.
Garden	1·6551	,,	1·6552	,,
Field	1·744	,,	1·776	,,

These numbers indicate the magnitude of the experimental errors in independent determinations of nitrogen in homogeneous soils.

C. H. B.

Estimation of Nitrates by Kjeldahl's Method. By M. A. Scovell (*Bull. U.S. Dep. Agric.*, **16**, 51—54).—The results of Jodlbaur's phenolsulphonic acid modification (Abstr., 1886, 834) are apt to be somewhat low. The author, substituting 2 grams of salicylic acid for the phenolsulphonic acid, obtained numbers of almost theoretical accuracy, both with pure nitrates and with mixtures made to represent fertilisers.

M. J. S.

Estimation of Phosphoric Acid. By G. Linossier (*Bull. Soc. Chim.*, **50**, 353—354).—The solution of the phosphate acidified with nitric acid and free from hydrochloric and sulphuric acids, is heated nearly to boiling and treated with an excess of bismuth nitrate; the clear, supernatant liquid is decanted on to a filter and the precipitate washed several times with boiling water; the filter is washed with a saturated aqueous solution of hydrogen sulphide, the mass of the precipitate treated in the same manner, and well shaken with the saturated hydrogen sulphide solution; the clear liquid is filtered and the residue again treated with hydrogen sulphide. Finally the bismuth sulphide is put on to the filter and washed with the hydrogen sulphide solution until the filtrate no longer shows a reaction with Poirrier's orange. The filtrate is boiled and the phosphoric acid determined with decinormal soda solution, using Poirrier's orange 3 as indicator. For very exact determinations, a second flask of the same size and containing the same amount of water and indicator should be used for comparison. (Compare this vol., p. 75.)

N. H. M.

Estimation of Carbon in Iron, Steel, &c. By T. W. Hogg (*Chem. News*, **58**, 199).—The borings are covered to a depth of about half an inch with concentrated cupric chloride, considerable excess of strong ferric chloride added, the mixture stirred for five minutes, heated gently to boiling, and acidified with a few drops of hydrochloric acid; the carbonaceous residue is then collected and treated as usual. When silicon is also present, the carbon should be filtered as soon as the decomposition is complete. The cupric and ferric chloride solutions should be neutral; the latter is added to prevent the formation of cuprous chloride which is objectionable from the difficulty of keeping it in solution.

D. A. L.

Volumetric Estimation of Zinc Oxide. By R. BENEDIKT and M. CANTOR (*Zeit. angew. Chem.*, 1888, 236—237).—Contrary to the statement of Classen, zinc oxide and carbonate can be accurately titrated with standard acid and alkali, using methyl-orange as indicator, and zinc salts using phenolphthaleïn. The oxide or carbonate is dissolved in excess of acid and the excess titrated back by soda solution. Zinc salts are dissolved in water (50 c.c. to 0·1 gram ZnO), phenolphthaleïn is added, and then standard soda solution to intense red colour. A few more c.c. of soda is then added, the mixture is boiled for some minutes, and the excess of soda titrated. If either free acid or zinc oxide is present in the zinc salt, it is neutralised in presence of methyl-orange by alkali or acid, as the case may be.

M. J. S.

Estimation of the Percentage of Lead in Tin-Lead Alloys by taking the Specific Gravity. By C. WINKLER (*Chem. Zeit.*, **12**, 1229—1231).—The author describes a simple apparatus for measuring the water displaced by the immersion of the object when determining the sp. gr. He recommends the use of such determinations, when made with some hundreds of grams of material, for the estimation of the proportion of lead in tin-lead alloys. D. A. L.

Estimation of Copper by the Iodide Method. By R. WILLIAMS (*Chem. News*, **58**, 272).—The author finds this method both expeditious and accurate in the case of refined or of pure copper; but impurities such as lead, iron, and arsenic are prejudicial. Ferric acetate and nitrate liberate iodine from the potassium iodide; arsenic acid also quickly decomposes that salt. D. A. L.

Separation of Manganese and Allied Metals from the Sesquioxide-group and Phosphoric Acid. By C. MEINEKE (*Zeit. angew. Chem.*, 1888, 219—232).—In the analysis of ferruginous materials, the determination of manganese, calcium, and magnesium, as also of small quantities of copper, nickel, cobalt, zinc, and barium, is of frequent occurrence. It is usual to separate from these the iron, aluminium, and phosphoric acid in a single operation. As the bulkiness of the precipitate renders complete washing tedious, it is recommended to adopt partial filtration and to take a measured portion of the filtrate. If, as is usually the case, the liquid is filtered hot, the temperature must be taken at each measurement and the volumes corrected. Müller employs flasks with the necks so graduated as to measure off three-fourths of the original solution, allowing at the same time for the bulk of the precipitate and for a fall of temperature from 90° to 80°. Test analyses show that the corrections so made can be depended on.

Precipitation of the Iron, &c., by Alkaline Acetates.—The conditions for the successful separation of manganese from iron by a single precipitation, are the neutralisation of the solution as perfectly as possible, the use of only small quantities of acetates and acetic acid, and a rapid but short boiling. A little iron usually remains unprecipitated. Müller, for the analysis of spiegeleisen and ferromanganese, dissolves 1·92 grams in 16 c.c. of hydrochloric acid (1·12) and 5 c.c. of nitric acid (1·2), adds ammonium carbonate until a permanent precipitate is obtained, dissolves this by 10 drops of hydrochloric acid, adds 5 c.c. of ammonium acetate (glacial acetic acid neutralised with ammonia of 0·96 sp. gr.), with 1 c.c. of glacial acetic acid, dilutes to 500 c.c., and heats to boiling. Taking three-fourths of the solution as above, and precipitating the manganese by hydrogen dioxide, he weighs as manganoso-manganic oxide, of which 0·1 gram corresponds with 1 per cent. of manganese. By using these proportions, a rather large amount of iron remains unprecipitated, but it very exactly compensates for the loss due to the unexplained fact that three-fourths of the solution contains only on an average 73·7 per cent. of the manganese. The manganese precipitate always contains nickel and cobalt. As the amount of these is fairly constant, a deduction of 0·2 per cent. is made in the case of 10 per cent., and 0·24 for 20 per cent. of manganese. The determination can be completed in three-quarters of an hour.

Precipitation of the Iron by Neutralisation with Ammonium Carbonate and Boiling.—The solution must be free from sulphates. Ammonium carbonate is added until the liquid just loses its transparency, and it is then heated to boiling. Partial filtration of the hot liquid is advisable, as the precipitate cannot be completely washed without some iron dissolving. Copper, cobalt, nickel, manganese, zinc, calcium, magnesium, and barium are almost perfectly separated from iron and aluminium by this method. In the case of the three last, a little ammonia should be added after the boiling, and boiled out again; the basic ferric chloride is thus converted into hydroxide, which can be washed. In presence of copper, this addition is inadmissible, and it also occasions the loss of a trace of manganese. Without it, traces of iron remain in solution.

Precipitation by Alkaline Sulphates.—The liquid is neutralised with ammonia and ammonium carbonate until a small permanent precipitate forms, leaving the solution still of a deep brown colour and feebly acid. On now adding ammonium sulphate, the iron is thrown down at ordinary temperatures as basic sulphate. Manganese, copper, nickel, cobalt, and zinc remain entirely in solution. Aluminium is partially precipitated. To remove it completely, together with any traces of iron still in solution, a few drops of ammonium acetate should be added and the liquid boiled.

Fritzsche adds to the feebly acid solution a small quantity of sulphuric acid, and then sodium hydrogen carbonate so long as this produces a brown precipitate of basic ferric sulphate. Särnström omits the sulphuric acid, with the advantage that the liquid remains clear to within a few drops of complete neutralisation. The basic ferric chloride separates suddenly and completely, whilst manganese is not thrown down by an excess of the reagent as long as the liquid shows the faintest acidity. In the presence of more than traces of aluminium, this and Fritzsche's method are inapplicable. Calcium and magnesium can be perfectly separated from iron by this method; barium only when in small proportion. For preparing the manganese solution for volumetric determination, this method does not appear preferable to Volhardt's zinc oxide process (Abstr., 1880, 143), but for gravimetric analysis the author regards it as the most advantageous yet brought forward. To prevent the manganese precipitate from containing alkali, it should be heated with ammonia and ammonium chloride for some time before filtering. M. J. S.

Estimation of Chromium by Hydrogen Peroxide. By A. Carnot (*Compt. rend*, **107**, 948—949).—It is well known that with solutions of chromic acid, hydrogen peroxide produces a fugitive, deep blue colour, which according to Moissan has the composition CrO_3,H_2O_2. When decomposition takes place, the solution contains a quantity of sesquioxide equivalent to the hydrogen peroxide decomposed.

The chromate or chromic acid solution is diluted to about 50 c.c., and nearly neutralised, the reaction being left acid. Commercial hydrogen peroxide diluted with 5 to 20 volumes of water is run into the liquid from a burette. A dark coloration is produced which turns blue and then green. The titration is ended when the blue coloration is no longer produced as a drop of the peroxide falls into the liquid. The same operation is repeated with a standard solution of pure potassium dichromate. It is advisable that the conditions in the two titrations should be as nearly identical as possible. If the solution is too concentrated, the green colour of the reduced chromium masks the blue coloration. C. H. B.

Analysis of Commercial Scheelite. By K. Rusag (*Chem. Zeit.*, **12**, 1316).—The following method of decomposing scheelite is recommended, as by it all inconvenience from silica is avoided. The finely pulverised mineral is heated with hydrochloric and hydrofluoric acids until the silica and excess of hydrofluoric acid are removed, the residue is moistened with fuming hydrochloric acid, and after a little while heated with plenty of hot water. The precipitated tungstic acid is washed, dissolved in ammonia, ammonium chloride added, and the solution filtered. The filtrate is evaporated to dryness with ammonium chloride, redissolved, and again evaporated to dryness with ammonium chloride; these operations are then repeated once or twice more, and the residue is ultimately ignited, at first below a red heat, but finally strongly. The tungstic acid obtained in this manner is of a pure yellow colour, and although it dissolves incompletely and with difficulty in ammonia, it nevertheless yields a sodium tungstate completely soluble in water, and from which neither silica nor alumina are deposited when the solution is boiled with ammonium chloride.

D. A. L.

Volumetric Estimation of Antimonious and Arsenious Acids. By A. Jolles (*Zeit. angew. Chem.*, 1888, 160—163).—Antimonious acid is completely oxidised to antimonic acid by an alkaline solution of potassium manganate, according to the equation $Sb_2O_3 + 2K_2MnO_4 = Sb_2O_5 + 2K_2MnO_3$. The oxidation of arsenious to arsenic acid is precisely analogous. The manganate solution may contain 4 or 5 grams of potassium manganate and 8 or 10 grams of potash in the litre. It is standardised by a solution of tartar emetic containing 10 grams in a litre or by a solution of arsenious acid in dilute hydrochloric acid. The titration is performed by simply running in the antimony or arsenic solution to a measured volume (5 or 10 c.c.)

of the manganate, with shaking, until the green colour changes to a clear yellowish-brown. Only after a time does the solution become turbid from separation of manganese dioxide. Substances in which the antimonious acid is to be determined are dissolved in hydrochloric and tartaric acids, diluted to a known volume (200 c.c. to each gram), and employed in the same way, taking care to keep the mixture strongly alkaline. The manganate solution should be freshly prepared, as it does not keep well. M. J. S.

Volumetric Estimation of Antimonic Acid. By G. v. KNORRE (*Zeit. angew. Chem.*, 1888, 155—157).—Weil's method (Abstr., 1879, 276) is rapid, but only approximate, owing to the difficulty of ascertaining the exact point at which the green colour of the cupric chloride disappears. Weller's process is based on the reduction of antimony pentachloride to trichloride by heating with potassium iodide, and estimation of the liberated iodine. The antimonic acid or salt is boiled with hydrochloric acid and potassium iodide in Bunsen's chlorine distillation apparatus until the mixture becomes colourless, the iodine being received in cold potassium iodide. In the absence of other oxidising agents, the method yields good results.

Herroun (Abstr., 1882, 661) adopts the same reaction, but omits the distillation. The author finds, however, that in the cold the reaction is either incomplete or very slow, since after decolorisation with thiosulphate, free iodine again appears in the liquid. Neither can satisfactory results be obtained when antimonic acid is reduced by boiling with hydrochloric acid and potassium iodide until the free iodine is all expelled, and then titrating the solution with standard iodine after addition of sodium hydrogen carbonate. Fleischer (*Lehrb. der Titrirmethode*, 2nd ed., 306) recommends reduction with sulphurous acid and subsequent titration with iodine. Complete reduction could not be effected in an open basin. The following process is, however, satisfactory:—The antimonate, strongly acidified with hydrochloric acid, is treated in a roomy flask with strong solution of sodium sulphite added gradually in small portions. It is then vigorously boiled until the sulphurous acid is expelled. A drop of phenolphthaleïn is added and then potash until the red colour appears. This is removed by a small excess of tartaric acid; sodium hydrogen carbonate is then added, and the liquid is titrated with iodine.

M. J. S.

Estimation of Nitrates in Natural Waters. By S. C. HOOKER (*Ber.*, 21, 3302).—One part of nitric acid in two millions gives, under certain conditions, a green coloration with a sulphuric acid solution of carbazole (compare Gräbe and Glaser, this Journal, 1872, 302). This reaction can be employed for the estimation of nitrates in natural waters as follows:—A measured quantity of the water (2 c.c. or less according to circumstances) is mixed with about 4 c.c. of concentrated sulphuric acid, and a small quantity of a sulphuric acid solution of carbazole added to the cold mixture. The coloration is then compared under exactly similar conditions with that produced by various quantities of a solution of potassium nitrate of known strength.

This method, and the precautions to be observed in presence of chlorides, nitrites, &c., will be fully described in a subsequent paper.

F. S. K.

Estimation of Acetone in Methyl Alcohol. By J. MESSINGER (*Ber.*, **21**, 3366—3372).—Krämer's method of estimating acetone in methyl alcohol by weighing the iodoform obtained on treating the sample with aqueous potash and iodine solution (Abstr., 1880, 826) is not only somewhat tedious and troublesome, but also gives results which are too high when the quantity of acetone present is small. A rapid and trustworthy method has been devised by the author, who estimates volumetrically the amount of iodine required to convert the acetone into iodoform. 20 c.c., or, if much acetone is present, 30 c.c. of normal potassium hydroxide solution and 1 to 2 c.c. of the methyl alcohol are shaken together in a stoppered flask, and 20 to 30 c.c. of one-fifth normal iodine solution is run in, and the whole shaken for 15 to 30 seconds until the solution becomes clear; it is then acidified with hydrochloric acid (sp. gr. = 1·025), an excess of decinormal sodium thiosulphate added, and finally titrated back with the iodine solution, starch being used as an indicator. The calculation is based on the equation given by Orndorff and Jessel for the action of bleaching powder on acetone (this vol., p. 34), which when modified to represent the action of iodine in the presence of potassium hydroxide, indicates that 3 mols. of iodine are required to convert 1 mol. of acetone into 1 mol. of iodoform. Inasmuch as commercial potassium hydroxide almost invariably contains nitrite, it is necessary to correct for this, which can readily be done by adding a decigram or two of potassium iodide to 20 c.c. of the normal solution, and titrating the liberated iodine in the usual way. Results obtained by the use of the method are given in the paper. W. P. W.

Detection of Invert-sugar in the Presence of Cane-sugar by Means of Soldaini's Solution. By E. PARCUS (*Chem. Zeit.*, **12**, 1316).—For this purpose, 5 grams of sugar are directly dissolved in 50 c.c. of Soldaini's solution, or the latter is added to a solution containing 5 grams of sugar. To detect traces of invert-sugar, the second plan is the best, but the solution must not be too dilute; 10 grams of sugar are therefore dissolved in 50 c.c. of water, filtered, and 25 c.c. of the filtrate run into 50 c.c. of boiling hot Soldaini's solution, the mixture is then boiled over a naked flame for five minutes with frequent shaking, and filtered. If, however, clarification with lead acetate is desirable, 20 grams of sugar are dissolved in water, lead acetate is added, the whole made up to 50 c.c. and filtered. 25 c.c. of the filtrate is treated with sodium carbonate, to remove excess of lead, made up to 50 c.c., filtered, and then 25 c.c. of this filtrate is treated as in the above experiment. There is almost always a turbidity produced when the alkaline sugar solution is boiled with Soldaini's solution, therefore the filtered precipitate should be carefully examined for cuprous oxide to be sure that reduction has taken place. Fehling's solution gives no turbidity on boiling with solutions containing lime, but it is not suitable for the detection of small quantities of invert-sugar. D. A. L.

Indirect Analysis of the Sugar-beet. By D. Sidersky (*Ann. Agronom.*, **14**, 407—420).—The indirect analysis is usually made on the juice expressed after rasping, the chief determinations being made by taking the specific gravity of the juice, and determining the sugar in it by the polariscope after clarification with lead acetate. The sugar found is multiplied by the factor 0·95 to give the percentage existing in the root itself, but it is well known that the results so obtained do not always agree very well with direct estimations of the sugar in weighed samples of the root, made by the Scheibler-Soxhlet process. The indirect method, however, possesses so many points of convenience and advantage, that the author has sought carefully for the sources of error, with a view to make the results of the two methods harmonise. He shows from a number of sources that the factor 0·95 is very close to the truth, and that even in abnormal roots the proportion of juice to the total weight of root is not far enough from this to cause serious error. Next he shows that the optically active substances other than cane-sugar contained in the juice do not cause more than a very slight error, even if the positive and negative errors do not cancel each other. Next, that the precipitate caused by the lead acetate certainly augments the richness of the juice in sugar a little by diminishing its volume, but that to correct this it suffices to deduct 0·17 from the saccharine richness of the juice in the case of roots containing 12—15 per cent. of sugar. Finally, he traces the important source of error to the fact that the juice expressed from pulped or rasped roots is not the normal juice as it exists in the whole root, but that the torn cells easily yield up their juice at first, whilst the whole or closed cells retain theirs, and on increased pressure yield only an abnormal juice by extravasation through their walls. Accordingly, the expressed juice varies in composition both with the fineness of the rasping and with the amount of pressure used. As it is not possible to rasp so completely as to disintegrate every cell, nor on the other hand to press so strongly as to deprive every cell, torn or whole, of all its juice, the author proposes to rasp or pulp in the ordinary manner, and to extract the juice in a centrifugal machine without using any pressure. Much less juice is obtained, but this is of normal composition, as it comes from the torn cells only, and on taking its density with the Mohr-Westphal hydrostatic balance (the hydrometer is not sufficiently accurate), and its rotatory power in the polariscope after treatment with lead acetate, and applying the usual factors, results are obtained in close accordance with direct estimation of sugar made on the root. In 14 samples the greatest difference observed was 0·4 per cent. of sugar, whilst by the method of expression the differences ranged up to 1·4 per cent. Moreover, the "quotient of purity" of the juice obtained in the centrifugal extractor agrees much better with that of the juice actually obtained in the diffusion process than does that of the juice obtained by pressure.

J. M. H. M.

Estimation of Sugar in Beet by Digestion in Water. By L. Pellet, by J. Weisberg, by L. Battut, and by M. Clerc (*Bied. Centr.*, 1888, 777—786).—On a former occasion, Pellet recommended for the estimation of sugar by polarisation, that water be substituted for alcohol, as being simpler and cheaper; but in order to clear the liquid previous to polarisation, the addition of triplumbic acetate is necessary, and the influence of this addition on the rotatory power of the sugar, as also that of the alcohol as compared with water, is here discussed and experimented on by several writers.

J. Weisberg (*Oesterr. Ung. Zeit. Zucker-Ind*, 1887, 272) considers that pure aqueous solutions of saccharose may be mixed with much lead acetate without any effect on the rotation; this observation is confirmed by Muntz, who adds that no opacity is produced, whilst an alcoholic solution of sugar is affected by lead, the rotatory power being reduced 1° by the addition of 1 c.c. of lead solution. If, however, impure solutions of sugar (such as beet-juice) are examined, then the first portion of lead which precipitates impurities has no influence, but a further addition reduces the polarising power. In the case referred to, 2 c.c. of solution, added to 50 c.c. of root extract and alcohol, has no more effect than 0·55 c.c. in the polariscope, but 9 c.c. causes a reduction to the extent of 0·4°, consequently only so much lead should be added as is sufficient to precipitate all impurities, and to facilitate this result a definite solution of triplumbic must be employed; it is prepared as follows: 600 grams of lead acetate, and 200 grams of lead oxide are dissolved in water to 29° Baumé (Weisberg), or treated with 2 litres boiling water, filtered, and brought to 30° Baumé (Pellet).

As before stated, Pellet finds that the extraction of beetroot mash may be as well performed with water as with alcohol, and considers that the differences which have been observed by other experimenters is due to their having added too much lead solution to the alcoholic, and too little to the aqueous extract; moreover, he considers it necessary to destroy all alkalinity of the alcoholic extract by acetic acid; the same holds good for the aqueous extract. Pellet further states that the sugar may be all extracted by cold water and lead solution, but the roots must be very finely pulped; this process of extraction in the cold is termed by Pellet "the method of the future," and his directions are as follows: 26·048 grams of the finely pulped roots, the particles of which must not exceed $\frac{1}{2}$—$\frac{3}{4}$ mm., are mixed with water and 3—6 c.c. of the lead solution above referred to, and after a thorough shaking, and addition of 0·5—6 c.c. of ether, the whole is made up to 200·7 c.c., filtered, acidified with a few drops of acetic acid, and then polarised in a 400 mm. tube. Unripe or abnormal beets require more lead. This process only occupies three minutes. M. Clerc (*Deut. Zucker-Ind*, 1888, 1114) approves of Pellet's methods. L. Battut (*Suc. Belg.*, 1888, 458) recommends the substitution of milk of lime and carbonic anhydride for much of the lead, but the process is much more complicated than those given by Pellet. E. W. P.

Estimation of Milk-sugar in Milk by the Polariscope. By P. Vieth (*Analyst*, 13, 63—65).—The results are practically the same, whether the proteïds are precipitated by Schmoeger's basic lead acetate method, or by the simpler plan of adding mercuric nitrate and filtering. With the latter reagent, a clear whey is obtained, even from cream containing 50 per cent. of fat and only 2·25 of proteïds.

The following rule is given for making the calculation. To 50 c.c. of the milk, add 1·5 c.c. of the mercuric nitrate. As the precipitated proteïds occupy 1·5 c.c., the strength of the sugar solution remains unaltered. The formula $\frac{p(93-f)}{93s}$, in which p = percentage by volume of milk-sugar as shown by the polariscope, f = percentage by weight of fat, and s = sp. gr. of the milk (water = 1), then gives the percentage by weight of crystallised milk-sugar in the milk. From this is to be deducted one-twentieth for water of crystallisation.

M. J. S.

Compounds of Starch with the Alkaline Earths. By C. J. Lintner (*Zeit. angew. Chem.*, 1888, 232—236).—Starch is completely precipitated from a dilute solution by a solution of lime in sugar syrup. Dextrin is not so precipitated. The composition of the precipitate varies according to the quantity of lime added, the observed extremes being 0·3164 and 0·0952 of lime for 1 of starch, corresponding approximately with the formulæ $C_6H_{10}O_5,CaO$ and $(C_6H_{10}O_5)_4,CaO$ respectively. The behaviour of baryta-water is precisely similar. Whether with or without alcohol (in the former case following accurately the instructions given by Asboth, Abstr., 1887, 868) the larger the quantity of baryta added, the greater the proportion precipitated by the starch. The precipitate varied in composition from $(C_6H_{10}O_5)_2,BaO$ to $(C_6H_{10}O_5)_8,BaO$. Dextrin is also precipitated by baryta in presence of a little alcohol.

Strontia-water and solutions of strontia in syrup precipitate starch completely only on addition of alcohol. The composition of the precipitate is variable in this case also. Therefore, for quantitative determinations of starch, the alkaline earths cannot be employed directly with sufficient certainty. (Compare Spence, Abstr., 1888, 632; Monheim, 1888, 1134; also Seyfert, *ibid.*) M. J. S.

Adulteration of Vegetable Fatty Oils. By W. Peters (*Arch. Pharm.* [3], **26**, 857—893, and 905—918).—The paper gives a detailed survey of the methods proposed for the detection of mixtures of various fatty oils, and freely quotes numerical results obtained by previous investigators. The author then details his own experiments on some of the methods surveyed, and recommends the following course for the detection of adulteration:—(1.) The melting point should be determined of the fatty acids insoluble in water, separated by hydrochloric or dilute sulphuric acid after saponification. With pure olive oil, the end-point of the melting varies between 24° and 29°. If the melting point of an olive oil is above 29°, we may presume that cotton-seed oil is present; if under 24°, the admixture of linseed, castor, or poppy oil may be assumed. (2.) Sesame oil is easily detected in olive and almond oils, by the beautiful green coloration obtained when the oil is treated with a mixture of equal parts of concentrated nitric and sulphuric acids; or by mixing the oil with 23 to 24 per cent. hydrochloric acid, in which 2 per cent. of cane-sugar has been dissolved, when the mixture becomes reddish after a couple of minutes, gradually passing to dark cherry-red; or, according to Langlies, 3 grams of the oil is warmed with 1 gram of a mixture of

3 parts of nitric acid (sp. gr. 1·38) and 1 part of water; in presence of 5 per cent. of sesame oil, the mixture takes a characteristic red colour. Cotton-seed oil is detected by agitating with 2½ parts of colourless nitric acid (sp. gr. 1·4); on cooling a brown colour is produced; or 2 c.c. of the oil is treated with two or three drops of a syrupy solution of antimonious chloride, when cotton-seed oil becomes chocolate-coloured with evolution of much heat, and in a short time solidifies. Oils of the Cruciferæ are detected by the reduction of an alcoholic solution of silver nitrate. (3.) The elaïdin test detects the presence of cotton-seed, sesame, and peach-kernel oils in olive oil by the various colours produced. 10 c.c. of oil is placed in a stoppered flask with 1 c.c. of nitric acid (sp. gr. 1·4) and 0·4 gram of metallic copper in splinters; on shaking, the red vapours are absorbed, and when cooled to 10° or 20°, olive oil becomes a solid white mass within 30 minutes, sesame oil becomes red, and the other two red to brown; the time of solidification is less definite than the colour produced. (4.) After saponifying and treating with mineral acid, to separate the organic acids, the different solubility of these in an equal volume of 90 per cent. alcohol gives important information. The alcoholic solution obtained from olive and almond oil remains clear after evaporating off half the alcohol and cooling to 20°, whilst that of earth-nut oil becomes turbid and cotton-seed oil becomes solid. (5.) The "iodine number," as determined by Hübl (Abstr., 1884, 1435—1437), is important. J. T.

Action of Sulphur Chloride on Oils. By C. A. FAWSITT (*J. Soc. Chem. Ind.*, 7, 552—554).—The heat reaction between certain oils and sulphur chloride being more marked than that obtained when sulphuric acid is used, the author made a series of experiments to see if characteristic results could be obtained which might be turned to some account as a test for oils. 30 grams of oil was weighed in a small beaker, which was then placed in a larger beaker, and the intervening space filled with cotton-wool. The temperature of the oil having been taken, the chloride was added slowly during constant stirring, and the time having been noted, the thermometer was kept stationary until the temperature ceased to rise, when it was noted and also the time. No difficulty was experienced in carrying out the trials except in the case of castor oil, which, owing to its high viscosity, could not be mixed intimately and sufficiently rapidly with the sulphur chloride, to prevent local action.

The majority of the oils used in the trials were compounds of fatty acid with glycerol, on all of which the chloride acted. It was, however, found to have little or no action on glycerol and stearic acid, but with oleic acid it shows a heat reaction similar to that with olive oil. In some cases hydrogen chloride was liberated, for instance, with palm oil, cod-liver oil, castor oil, rosin oil, and mineral oils, whilst in others, such as seal oil, rape oil, and olive oil, no gas was given off. The evolution of gas had, in some cases, a marked effect in stopping the rise in temperature, notably in the case of mineral oils and rosin oil. In all cases, with the exception of palm oil, which appeared to turn thinner, the oils were thickened by the sulphur chloride treatment, and when the higher proportions were used the product was usually solid.

D. B.

Detection of Margarin in Butter. By V. PLANCHON (*J. Pharm.* [5], 18, 482—489).—The author has devised a process by which the whole work is done on one portion of the sample, and by which he determines the equivalent of saponification, the soluble acids and the insoluble acids. Three standard solutions are required for the process: a semi-normal sulphuric acid solution, a normal alcoholic sodium hydroxide solution, and a one-fifth normal aqueous solution of sodium hydroxide. The butter is heated to 50°, and 5 grams of the clear fatty matter is weighed off into a tared flask, capable of containing 150 c.c. of water, containing 15 per cent. alcohol when heated to 50—55°, and having the mark at the bottom of the neck. 25 c.c. of the alcoholic soda solution is added and boiled 20 minutes with a reflux condenser, when the saponification is almost complete; after cooling a little, about 60 c.c. of water is added, and some drops of phenolphthaleïn and standard acid is run in to neutralisation; the amount is noted. Then more acid is added until the exact equivalent of the soda taken has been used, and the flask is heated at 50—55°, when the fatty acids fuse, and after shaking a few times, warm water is added to bring the lower level of the acid layer up to the mark on the flask. After vigorously shaking, the flask is cooled, and 100 c.c. of the liquid passed through a tared filter dried at 100°, is titrated with the aqueous sodium solution; this gives the soluble acids. On adding boiling water to the tared flask, the fatty acids can be easily passed on to the tared filter and washed, after which the filter and its contents are dried at 100° for six or seven hours, when the loss of weight will not exceed 5 or 6 mgrms. per hour.

Calculation of results. 1. *Equivalent of saponification.*—The number of c.c. of acid equivalent to the sodium solution required for saponification, multiplied by 0·4, gives the weight in grams of sodium hydroxide required to saponify 100 grams of the sample. For pure butter this is about 16·12 to 16·4, and for margarin it is about 13·92 to 14·16. 2. *Soluble acids.*—The equivalent in butyric acid per 100 grams of sample is obtained by multiplying by the coefficient 0·528, the number of c.c. of one-fifth aqueous soda solution required to neutralise the 100 c.c. of solution obtained. For the samples of pure butter examined, this amounts to 3·85 to 4·41; and for margarin, 0·16 to 0·26. 3. *Insoluble acids.*—The weight of dried fatty acids is multiplied by 20. For pure butter this becomes 87·62 to 88·0; and for margarin 95·40 to 95·76.

The coefficient of saponification and the proportion of soluble acids can easily be determined in less than an hour, and this information is generally sufficient to show the degree of purity of the sample. A series of mixtures of butter and margarin, examined as above, gave results not more than 2 per cent. wide of the truth. J. T.

The Iodine Absorptions, combining Weights and Melting Points of some Fatty Acids. By R. WILLIAMS (*Analyst*, 13, 88—89).—The following are the average results from several samples of each kind of fat or oil:—

	Iodine absorption.	Combining weight.	Melting point.
	per cent.		
Tallow	41·3	276	119° F.
Lard	64·2	296	100
Cotton-seed oil	115·7	289	96
Olive oil	90·2	286	81
Linseed oil	178·5	283	75
Rape oil	105·6	307	71
Castor oil	93·9	292	—
Cocoanut oil	9·3	201	75
Palm oil	53·4	263	114
Sperm oil	88·1	305	56

M. J. S.

Detection of Cotton-seed Oil in Lard. By A. H. ALLEN (*Analyst*, **13**, 161—165).—Solid neutral fats and fatty acids from cotton-seed oil are used in the adulteration of lard. Their presence does not appreciably affect the melting and solidifying points. The specific gravities (at 99°) are as follows:—Cotton-seed fat, 0·8684; cotton-seed oil, 0·8725; acids from cotton oil, 0·8476; lard, 0·860—0·862; fatty acids from lard, 0·8372—0·8385.

The following are the percentage iodine absorptions (Hübl's method):—Cotton-seed fat, 89·8; cotton-seed oil, 108—110; acids from cotton oil, 115·8; lard, 55·4, 60·5, and 62 (Allen), 46·57, 51·2, 51·5, and 55 (other experimenters). Detection or determination by means of the difference in the iodine absorption may, however, be counteracted by the presence of beef suet, which has a much lower iodine absorption. Its sp. gr. is, however, identical with that of lard, so that an approximate determination can be effected by combining these two features. Milliau's modification of Bechi's silver nitrate test, appears to be valuable as a qualitative method (compare Abstr., 1888, 633, 1349). M. J. S.

Mixed Lard and the Detection of Cotton-seed Oil. By O. HEHNER (*Analyst*, **13**, 165—167).—The commission appointed by the Italian Government to investigate Bechi's method (Abstr., 1888, 301) reported that it is perfectly trustworthy, provided the reagent contains a little pure nitric acid, and the oil to be tested has been filtered. The reagents recommended are composed as follows:—(No. 1.) Silver nitrate, 1 gram; alcohol (98 per cent.), 200 grams; ether, 40 grams; nitric acid, 0·1 gram. (No. 2.) Amyl alcohol, 100 grams; colza oil, 15 grams. 10 c.c. of the oil is mixed with 1 c.c. of No. 1 and 12 c.c. of No. 2. The mixture is shaken and heated on the water-bath for a quarter to half an hour. In presence of cotton oil, it darkens from reduction of silver. With too little free acid present, reduction may occur in the absence of cotton oil; with too much, it may not take place even with cotton oil. The author sees no advantage in Milliau's modification, and omits the amylic solution of colza oil as unnecessary. He adds one volume of the silver solution to two volumes of the oil and heats for 15 minutes.

Maumené's reaction furnishes a quantitative method. 50 grams of pure lard mixed with 10 c.c. of strong sulphuric acid give a rise of 24° to 27·5°; cotton-oil a rise of about 70°. Mixtures with known proportions gave results agreeing closely with the calculated numbers.

Salkowski's phytosterin test (Abstr., 1888, 201) affords valuable corroboration. M. J. S.

Adulteration of Lard with Cotton-seed Oil. By R. WILLIAMS (*Analyst*, 168—169).—Koettstorfer's test is useless, since both fats require the same amount of alkali. The melting point of lard depends so much on the part from which the fat is taken as to be no criterion of purity. The sp. gr. can only furnish indications when the proportion of cotton-seed oil is large. Maumené's test has failed in the author's hands. The iodine absorbtion test is the most trustworthy; genuine American lards absorb 60 to 62 per cent.; a sample of leaf lard rendered by the author absorbed 51·8; whilst refined cotton oil absorbs 110, and beef stearin, on the other hand, only 21.

Milliau's silver nitrate test appears to be characteristic for cotton oil. Of numerous other oils and fats, none exerted a reducing action. M. J. S.

Lard Adulterated with Cotton-seed Oil. By E. W. T. JONES (*Analyst*, **13**, 170—171).—The sulphur chloride reaction will detect any important adulteration with cotton oil with certainty. 5 grams of the lard is melted in a porcelain basin, and just before it solidifies there is added to it ·2 c.c. of a mixture of equal volumes of carbon bisulphide and sulphur monochloride. This is well stirred in, and the mixture allowed to stand at the ordinary temperature. Pure lard thickens somewhat in the course of three hours, but mixtures containing cotton oil become quite hard in half that time (see also Warren, Abstr., 1888, 1348).

The author describes his mode of performing Hübl's test. The reagent is made by dissolving separately 5 grams of iodine and 6 grams of mercuric chloride, each in 100 c.c. of 95 per cent. alcohol, mixing and allowing to remain for 12 hours before use. About 0·5 gram of the fat is dissolved in 10 c.c. of chloroform in a stoppered bottle, 20 c.c. of Hübl's reagent is added, and the mixture left in the cold for three hours. The contents of the bottle are then rinsed into a beaker with potassium iodide solution, and the unabsorbed iodine is titrated by thiosulphate. The numbers reported for genuine commercial lard are:—Highest 61·31, lowest 56·47, average 58·9. The author adopts the number 60, and for cotton oil 105.

The average sp. gr. of the same samples of lard (at 100° F.) was 0·906, that of cotton oil was 0·9135. The percentage of adulteration calculated from the results of the two methods agreed closely. M. J. S.

Adulteration of Lard with Cocoa-nut Oil. By A. H. ALLEN (*Analyst*, **13**, 189—190).—The author has met with a specimen of lard adulterated with cocoa-nut oil. The following values are given:—

	Lard.	Cocoa-nut oil.	Suspected sample.
ORIGINAL FAT:—			
Plummet gravity at 99°	0·860—0·861	0·868—0·874	0·8666
Iodine absorption	55—61	9	37·4
Saponification equivalent	286—292	209—228	265·2
$\frac{N}{10}$ alkali required by distillate from 5 grams	0·5	7·0	3·3
SEPARATED FATTY ACIDS:—			
Plummet gravity at 99°	0·838—0·840	0·844	0·840
Iodine absorption	61—64	15·01	42·5
Mean combining weight	278	200	253·04

The volatile acids from the suspected sample had the odour of the distillate from cocoa-nut oil, and were in part insoluble. The silver nitrate test gave a negative result. The saponification equivalent furnishes the most accurate indications of the percentage adulteration, and would be unaffected by the presence of cotton-seed oil or tallow.

M. J. S.

Analysis of Grease. By L. ARCHBUTT (*J. Soc. Chem. Ind.*, 7, 494—495).—The method, which has for its object the separation and estimation of fatty acids in the presence of neutral fat and oil, consists in dissolving the mixture in ether and shaking with weak alcoholic soda, which extracts all substances of acid character, and leaves the mineral or other neutral oil dissolved in the ether.

The author has verified the method by experiment on tallow, palm oil, olive oil, and linseed oil. His trials with colophony were not, however, successful, and seem to confirm Allen's observation regarding the probable presence of either ethers or anhydrides in colophony, which do not react with caustic potash unless heated therewith.

D. B.

Estimation of the Oil and Water in Linseed Cake. By P. BAESSLER (*Landw. Versuchs-Stat.*, 35, 341—349).—In previous volumes of the *Landw. Versuchs-Stat.* (32, 1; 34, 420, 460), it has been stated that in determining the fat in foods, all water should first be expelled by drying at 100°, such treatment, however, in the case of linseed cake leads to serious error. Samples of two different cakes were taken, and the oil determinations in portions dried in a vacuum over sulphuric acid, namely, 7·69 per cent. in one cake and 9·96 per cent. in the other, were taken as correct; air-dried portions gave results 0·33 and 0·38 per cent. too high; portions dried at 100° for six hours gave results 3·95 and 2·26 per cent. too low; and portions dried at 105° for 10 hours gave results 5·13 and 4·55 per cent. too low. The following experiments showed that the error was caused by the absorption of oxygen by the oil of the cake with the formation of a substance insoluble in ether. Portions placed in a duck-shaped drying tube, immersed in boiling water, and connected with calcium chloride tubes were subjected to a current of dried air, and it was found that the loss of weight in the drying tube did not amount to as much as the gain in the calcium chloride tubes, showing that something had been absorbed from the air. Brownish-yellow oily drops condensed in the calcium chloride tubes, so that the gain in these is not water alone. On extraction with dry ether, the cakes thus treated gave lowered percentages of fat. On repeating the experiment, using hydrogen instead of air, the loss in the drying tube was equal to the gain in the calcium chloride tubes, and on extracting with ether, the percentage of oil was the same as when the cake had been dried in a vacuum. The oil in this case was greenish-yellow, whilst that from cake dried by heating in air was brownish-yellow. To prove that it was the oil that suffered oxidation, some oil from cake dried in a vacuum was mixed in the drying tube with pumice in small grains, and on heating at 100° in a current of dry air was found to gain in weight and to give the brownish-yellow oily substance in the calcium chloride tubes; on extracting with ether for six hours, only 26 per cent. of the oil was removed. The behaviour of the insoluble residue with dilute potash was studied, and the author concluded that the oxidised oil being insoluble in ether, coats and protects some unaltered oil. To obtain correct results, therefore, the amount of water in the cake should be determined by drying either in a vacuum over sulphuric acid or in a current of dry hydrogen, and the oil determination should be made in the sample thus dried.

H. H. R.

Analysis of Wax. By G. BUCHNER (*Chem. Zeit.*, **12**, 1276).—Allen has shown that chemically bleached wax differs from wax bleached by exposure to sunlight, in having a greater sp. gr. and higher melting and solidifying points; the author now shows that when examined by Hübl's method it also has a higher percentage of acid (mean 23·01) and a higher saponification equivalent (98·36), whilst the ratio (1·32) of these numbers is lowered, the corresponding numbers for sun-bleached wax being 20, 95, and 1·37 respectively.

D. A. L.

Chemical Examination of certain Gums and Resins. By R. WILLIAMS (*Chem. News*, **58**, 224—225).—The author has examined some gums, &c., for total potash absorption, saponification equivalent, potash required to neutralise free acid, iodine absorption, loss at 100°, and ash. The gums he examined were amber, animi, arabic, asphaltum, benzoïn, bone-pitch, copal, damar, dragon's blood, elimi, gamboge, kaurie, mastic, rosin, sandarac, senegal, shellac, and tragacanth. The data are tabulated in the paper.

D. A. L.

Detection of "Saccharin" in Beer. By A. H. ALLEN (*Analyst*, **13**, 105—106).—A pint of the beer is concentrated to about one-third, acidified with phosphoric acid, and shaken with ether. The residue from the ethereal solution is fused with alkali and tested for a sulphate. Beer to which less than half a grain of Fahlberg's "saccharin" had been added gave distinct indications. The original beer gave no trace. One part of barium sulphate corresponds with 0·785 of "saccharin." The simultaneous presence of salicylic acid does not affect this mode of detection. M. J. S.

Estimation of Alkaloïds in Nux-vomica. By A. KREMEL (*Arch. Pharm.* [3], **26**, 899, from *Pharm. Post*, **21**, 534).—5 grams of the finely powdered nux-vomica seeds is treated in an extraction apparatus with 40 c.c. of a mixture of three parts of chloroform and one part of alcohol for two to three hours. The extract is agitated with 25 c.c. of 10 per cent. sulphuric acid, and again with 15 c.c. of the same acid, the acid solution is separated from the chloroform in a separating funnel, and made alkaline with ammonia, after which the free alkaloïd is shaken with 25 c.c. of chloroform. The chloroform solution is evaporated in a tared glass dish, and the residue is weighed. Numerous results obtained during the year have varied from 1·84 to 2·76 per cent., the average being 2·5 per cent. J. T.

Estimation of Quinine by Kerner's Method. By E. A. RUDDIMAN (*Chem. News*, **58**, 202—204; 216—218; 226—227).—The author has investigated the version of Kerner's test for quinine given in the U.S. Pharmacopœia, and finds, firstly, that it is not applicable to samples containing more than 2 per cent. of cinchonidine sulphate, inasmuch as the final clearing of the solution is indistinct and uncertain, and, moreover, the water used in the first instance is insufficient to dissolve all the cinchonidine salt. The following test for commercial quinine gives better results, and would include all samples coming within the officinal test:—1 gram of the sample is dissolved in 30 c.c. of boiling water, cooled, and digested at 15° for two hours; 5·26 c.c. of this solution should be both precipitated and re-clarified by 7 c.c. of ammonia, sp. gr. 0·960. In order to ascertain the relation of such a solution to those prepared in the ordinary manner, 12 experiments were made, and it was found on the average that 5 c.c. of solutions prepared by digesting 1 gram of quinine with 10 c.c. of water at 15° for three hours, corresponded with 5·26 c.c. of solutions obtained by dissolving 1 gram in 30 c.c. of boiling water, and then digesting at 15° for three hours; although the amount of ammonia actually required varied for each sample.

In another series of test experiments, the author shows that as the temperature at which the titration is made rises, the quantity of ammonia required decreases, the average diminution per degree C. being 0·148 c.c. and 0·172 c.c. respectively for ammonia of sp. gr. 0·920 and 0·960. Further experiments with solutions containing cinchonine sulphate in quantities varying from 0·005 to 0·05 gram per 50 c.c. of standard quinine sulphate solution, indicate that each 0·001 gram of $(C_{19}H_{22}N_2O)_2,H_2SO_4 + 6H_2O$, requires 0·36 c.c. of ammonia, sp. gr. 0·920, for its precipitation and re-solution, and, therefore, in titrations, any excess of ammonia above that required by the standard quinine solution is readily calculated to cinchonidine. The proportions of water recommended in the officinal test of the different forms of quinine are not exactly the same as in Kerner's original test; to conform with the latter, the proportions of water should be, for the free alkaloïd 11·7, for the acid sulphate 8·07, for the hydrochloride 10·895, for the hydrobromide 10·2, and for the dried sulphate 10·144. D. A. L.

Detection of Cochineal in Alimentary Substances. By E. LAGORCE (*J. Pharm.* [5], 18, 489—492).—The substance being dissolved in water or weak alcohol, is slightly acidified if necessary with a drop or two of acetic acid, and the colouring matter is extracted by agitation with amyl alcohol; in presence of excess of acid, the reaction is not produced. The amyl alcohol is decanted and evaporated in presence of sufficient water. The aqueous solution thus obtained is treated with some drops of a 3 per cent. solution of uranium acetate, when a beautiful bluish-green coloration, or a precipitate of the same tint, is produced. Acids destroy this colour with the production of the orange tint of carminic acid. In the case of wines, the amyl alcohol is mixed with an equal volume of benzene, or, better still, toluene, otherwise œnolic acid is also taken up by the amyl alcohol, and the cochineal may be completely masked. Ammoniacal cochineal, which has occasionally been employed to colour wine, behaves differently with uranium oxide; the lake produced is rose-violet or violet-blue. Other substances, however, give coloured lakes with uranium oxide; so that if, in the process given above, a violet-lake is produced, it will be necessary to prove the absence of logwood before asserting the presence of cochineal; to this end it is only necessary to remember that ether extracts a yellow substance from logwood solutions which becomes rose to reddish-brown on addition of ammonia, and black with potassium dichromate. J. T.

Detection of Urobilin in Urine. By GRIMBERT (*J. Pharm.* [5], 18, 481—482).—The urine is mixed with an equal volume of fuming hydrochloric acid heated, until it begins to boil, and after cooling is agitated with ether. This takes a pale brownish-red colour with a decided green fluorescence. Examined by the spectroscope, the ethereal solution gives the absorption-band of urobilin; on evaporation, a garnet-red residue remains which is soluble with fluorescence in chloroform, and without fluorescence in alcohol, glycerol, and acetone, but less soluble in water. The ethereal solution shaken up with an alkali loses its colour, whilst the alkali becomes deep-red. On acidifying this in presence of fresh ether, a yellow slightly fluorescent solution is obtained, which, however, still gives the absorption-band of urobilin; on evaporation, an orange-yellow residue is left. This method of detecting urobilin tends to confirm Jaffé's view that urobilin does not exist as such in urine, but is produced under the action of oxidising agents from some chromogenic substance not yet isolated. J. T.

General and Physical Chemistry.

Invisible Lunar and Solar Spectra. By S. P. LANGLEY (*Phil. Mag.* [5], **26**, 505—520).—The author having detected heat of very low refrangibility in the spectrum of the sun-lit moon, has succeeded in isolating it in direct sunlight, the difficulty being greater here, owing to the preponderance of heat of moderate wave-length. The solar bands of low refrangibility are greatly affected by the altitude of the sun and the season. As they recede from the visible spectrum, they become broader, and beyond 5μ merge into one broad band. At $10{\cdot}2\mu$ a maximum is observed only in cold weather, succeeded by a minimum. The greatest maximum occurs at 13 or 14μ, a distance from the visible spectrum of over 20 times its length; this band is identical with that observed in the moon's spectrum, and corresponds with the maximum radiations of melting ice. The points of minima in the spectrum are identical with the absorption-bands obtained from a copper surface at 100°, at a distance of 100 m. The amount of radiation is excessively small, and there is not the great discrepancy between this part of the solar and lunar spectra which is observed in the visible spectra. This part of the solar spectrum is not hotter than that of melting ice; hence it appears that the earth's surface, even when at 0°, gives out radiations which permeate the atmosphere. H. K. T.

Absorption-spectra of Blue Solutions. By F. B. PITCHER (*Amer. J. Sci.*, **36**, 332—336).—By means of a modified Glan's spectrophotometer, the author has examined various blue pigments, including ultramarine, indigo, prussian blue, and some commercial mixtures. The resulting observations are mapped in curves, the various pigments absorbing the rays between A and G irregularly; nevertheless each individual pigment gives a characteristic curve, which may possibly serve for its identification in mixtures. The colours of these pigments are therefore not as pure or saturated as the approximate hues in the longer waved portions of the spectrum. Acid litmus solution examined in like manner was marked by brightness in the red, almost complete transparency for rays between B and C, and slight minima at D and F; with neutral litmus, the brightness in the red disappears, the absorption at D is much increased, whilst the whole spectrum is only half as bright as before neutralisation; in alkaline litmus solution, the absorption in the yellow increases and extends, and the brightness of the whole spectrum is again diminished, especially in the red portions. Copper sulphate solution absorbs slightly in the red, showing a maximum transparency between E and F, but absorbs again towards G. When, however, ammonia is added to the solution, there is strong absorption throughout the orange and yellow, whilst the absorption between F and G practically disappears. D. A. L.

Relation between Rotatory and Refractive Powers of Chemical Compounds. Part I. By I. KANONNIKOFF (*J. Russ. Chem. Soc.*, 20, 1888, 571—578).—The author has determined very accurately the rotatory powers (α) and refractive powers (ϕ) of several organic substances at different degrees of dilution, and finds $\frac{\alpha-\alpha'}{\phi-\phi'} = \text{A} = \text{const.}$ After differentiation and subsequent integration, the following relation is obtained: $\alpha = \text{A}\phi + \text{B}$. For cane-sugar, A = 11·40 and B = −268·23 (267·68 to 268·71).—It is found that the constants A and B are not identical for substances of the same chemical composition and function; for example, with cane-sugar, milk-sugar, and maltose, or with dextrose and galactose. But it is interesting to find that the relation A = constant obtains, at least in the case of the sugars investigated by the author, the constant varying from 23·52 to 23·60. How far this value varies with other compounds and different solvents is a subject for further investigation.

The following relation between the constant B and the specific rotatory power $[\alpha]_D$ is found by the author:—

	Saccharose.	Lactose.	Maltose.	Galactose.	Dextrose.	Mean.
$B/[\alpha]_D =$	4·18	4·37	4·19	3·98	4·33	4·20

from which $[\alpha]_D = B/4{\cdot}2$. The same is seen in the case of A, for—

	Saccharose.	Lactose.	Maltose.	Galactose.	Dextrose.	Mean.
$[\alpha]_D/A =$	5·62	5·39	5·62	5·92	5·45	5·60

from which $[\alpha]_D = 5{\cdot}6 \times A$.

The results obtained by the author with the carbohydrates are arranged in a table, and it is shown that the refractive power may be calculated, with close approximation, from the rotatory power of any of the compounds in question. The author is continuing his investigations.

B. B.

New Theory of Molecular Volume and Refraction. By E. KETTELER (*Zeit. physikal. Chem.*, 2, 905—919).—The author points out the unsatisfactory nature of the expressions proposed for the molecular refraction, and suggests an equation of the form $(n^2-1)(1-\beta d)/d = \text{M}$, or $(n^2-1)(v-\beta) = \text{M}$, where β is the volume actually occupied by the ponderable molecules, v that of the space in which they are contained, $(v-\beta)$ being therefore that of the intermolecular ether, and M is a molecular function depending on the constitution of the medium. In the case of gases, where β becomes so small in comparison with v that it may be neglected, the formula becomes $(n^2-1)v = \text{M}_g = \text{const.}$, which is Newton's law. If the pressure were infinitely great, v would in its turn vanish, and the value of the expression simply depend on β. The true molecular volume of the substance is given by $\text{P}\beta$, where P is the molecular weight; the expression at present accepted for the molecular volume Pv being only the apparent volume, and including the space between the molecules occupied by the ether. M may have one of two values, both of which are definite physical constants, the one M_f being for the liquid, and the other M_g for the gaseous state.

The value of β may be obtained in three ways: by varying the temperature, the pressure, or the constitution of the media examined. In the first two cases, if v be known or determined as a function of temperature or pressure, and then for two different temperatures or pressures observations of n be made, we get by elimination of M from the two observations—

$$\beta = \frac{(n_1^2 - 1)v_1 - (n_2^2 - 1)v_2}{n_1^2 - n_2^2}.$$

In the third case, the author shows how by mixing the substance, the constants for which are unknown, with one the constants for which have been previously determined by one of the above methods, the unknown constants may be deduced by observations on different mixtures.

Particular stress is laid on the importance of the constant β, as giving a means of determining the true molecular volume Pβ of a compound. Values of β calculated from Weegmann's observations are given. H. C.

Kinetics of Substances in Solution. By M. LOEB and W. NERNST (*Zeit. physikal. Chem.*, 2, 948—963).—From determinations of Hittorf's ratio of transference and the conductivity of a number of silver salts, the authors have calculated the ionic velocity of silver, according to the principles laid down by Kohlrausch, with the view of still further testing the truth of the modern views on electrolysis. The constancy of the value obtained from observations with eight different salts gives satisfactory evidence for the truth of the theory, the numbers varying only within very narrow limits from a mean value of 591×10^{-8} at 25°.

The calculated values for the velocities of the other ions are also given, and it further appears from a comparison with the temperature coefficients of the velocities, that the latter decrease as the velocity increases. H. C.

Determination of the Basicity of Acids from the Conductivity of their Sodium Salts. By W. OSTWALD (*Zeit. physikal. Chem.*, 2, 901—904).—The author has further tested the principle laid down by him for determining the basicity of an acid from the conductivity of its salts (Abstr., 1888, 331), with a number of pyridine- and quinoline- carboxylic acids of different basicity, the highest being the pentacarboxylic acid of pyridine. He finds in every case a confirmation of the law that the increase in the molecular conductivity of the salt with an increase in the dilution from 32 to 1024 litres is equal to $10 \times n$, where n is the basicity of the acid.

H. C.

Heat of Combustion of Terpilene, Terpin Hydrate, and Terpin. By W. Louguinine (*Compt. rend.*, **107**, 1165—1167).

	M. p.	B. p.	Rot. power.	Heat of combustion		Heat of formation.
				Per gram.	Per gram-molecule.	
(1.) Inactive terpilene...	33°	—	—	9530·4	1467682	113318
(2.) Caoutchene hydrate	33	—	—	9578·7	1475120	105880
(3.) Active terpilenol....	—	—	−80°	9597·0	1478077	102923
(4.) Active terpilenol....	—	—	−80	9575·2	1474581	106419
(5.) Synthetical borneol..	33	—	—	9551·0	1470854	110146
(6.) Eucalyptol	—	175°	—	9481·3	1460120	120880
(7.) Terpin hydrate	—	—	—	7621·1	1448009	270991
(8.) Terpin	—	—	—	8455·6	1454363	195637

(1), Obtained by the action of dilute acid on terpin; (2), by the action of glacial acetic acid on caoutchene; (3), by the action of formic acid on French terebenthene; (4), by the action of glacial acetic acid at 100° on French terebenthene; (5), by the action of glacial acetic acid at 200° on French terebenthene.

It would seem that the last molecule of water in terpin hydrate is very loosely combined, but the formation of terpin from water and the hydrocarbon corresponds with a very considerable development of heat.

C. H. B.

Heats of Combustion of Camphors and Borneols. By W. Louguinine (*Compt. rend.*, **107**, 1005—1008).

	Rot. power.	M. p.	Heat of combustion.		Heat of formation.
			Per gram.	Per gram-molecule.	
Laurel camphor, dextrogyrate	—	—	9225·1	1402215	109785
Feverfew camphor	−41° 6′	175°	9302·8	1414026	97975
Racemic camphor	—	178·8	9298·7	1413402	98598
Dryobalanops borneol......	—	—	9510·85	1464671	116329
Valerian camphol	−37 7	208·8	9561·6	1472486	108514
Racemic camphol	—	—	9570·3	1473826	107174

It is evident that physical isomerism is accompanied by very slight differences between the heats of formation. The heat of formation of laurel camphor is almost identical with that of cymene, and it is well known that camphor is readily converted into cymene. Conversion of camphor into borneol by the addition of H_2 corresponds with 6544 cal. The hypothetical conversion of borneol into menthol by the addition of H_2 would correspond with 24671 cal., and the magnitude of this number indicates a possibility of actually realising this conversion.

C. H. B.

Heat of Dissolution of Anhydrous Lithium Iodide. By A. Bodisco (*J. Russ. Chem. Soc.*, 1888, 500—503).—The anhydrous iodide was obtained from the salts $LiI + 3H_2O$ and $LiI + 2H_2O$ by heating them nearly to dull redness in a current of hydrogen. The heat of dissolution was found equal to 14,886 cal. According to Thomsen, the heat of formation of Li + I + aq = 76,100 cal., so that the formation of LiI from its elements = 61,214 cal. Now as the heat of formation of Li_2O = 140,000 (Beketoff), or of a quantity equivalent to LiI = 70,000; this value is by 8,786 cal. larger than the heat of formation of LiI, whereas in the case of the other alkali metals the reverse is always found to be the case. This shows that there is no constancy of modulus, but that the energy of chemical reaction accompanying the formation of a compound depends on the relation of masses of the constituents, as shown by Beketoff.

B. B.

Density and Expansion by Heat of Saline Solutions. By G. J. W. Bremer (*Rec. Trav. Chim.*, 7, 268—309).—The densities of calcium chloride and sodium carbonate solutions at different temperatures have been most carefully determined, for temperatures above that of the outside air by means of a specific gravity bottle, and for temperatures below by means of a dilatometer. It is found that between 0° and 100° the variation of the density with temperature may be expressed by $d = d_0(1 + at - bt^2)$. The following values for a, b, and d_0 have been calculated for calcium chloride solutions:—

Grams $CaCl_2$ in 100 grams water.	b.	a.	d_0.
4·4295	0·000003301	0·0001126	1·03619
7·4966	0·000002727	0·0001649	1·05948
7·4913	0·000002697	0·0001672	1·06036
11·8658	0·000002092	0·0002231	1·09085
13·6023	0·000001751	0·0002480	1·10704
20·9280	0·000001218	0·0003125	1·15373
28·5534	0·000000961	0·0003262	1·20597
31·5326	0·000000871	0·0003425	1·22005

For sodium carbonate solutions the following values are given:—

Grams Na_2CO_3 in 100 grams water.	b.	a.	d_0.
3·2430	0·000002797	0·0001766	1·03551
4·8122	0·000002578	0·0002046	1·05171
7·4587	0·000002306	0·0002342	1·07677
10·1400	0·000002041	0·0002732	1·11192

It will be noticed that in each case a increases and b decreases with the concentration of the solution. Hence the greater the concentration the more will the curve representing concentration approximate to a straight line. The different curves will also intersect very nearly at the same point.

It is found that d_0 is a function of the amount p of anhydrous salt dissolved in q grams of water, such that $d_0 = (p + q)\ (\alpha p + \beta)$, where α and β are constants. The equation $d_0 = 1 + \alpha p + \beta p^2$, is found to be in better agreement with the observations. β is negative for calcium chloride and equal to zero for sodium carbonate. The coefficients of dilatation a and b may be represented in similar manner as functions of the concentration.

Curves for sodium carbonate do not show any break in continuity at 36°, where the solubility of the salt abruptly changes. H. C.

Dilatation of Salt Solutions. By N. TSCHERNAY (*J. Russ. Chem. Soc.*, 1888, **20**, 486—497).—In a former paper (this vol., p. 204) the author has described his experiments with solutions of nitrates of alkalis and alkaline earths. In the present paper, the dilatation of solutions of chlorides of the same elements was determined. The following values were obtained :—

$HCl + 50H_2O\ \ V_t = 1 + 0{\cdot}0000652t + 0{\cdot}000004355t^2$ (Marignac).
$LiCl + 50H_2O$ „ $= 1 + 0{\cdot}0000557t + 0{\cdot}000004036t^2$
$NaCl + 50H_2O\ \ 1 + 0{\cdot}0002318(t - 9{\cdot}8) + 0{\cdot}000003093(t - 9{\cdot}8)^2$.
$KCl + 50H_2O = 1 + 0{\cdot}0001239t + 0{\cdot}000003611t^2$.
$RbCl + 50H_2O = 1 + 0{\cdot}0001267t + 0{\cdot}000003716t^2$.
$MgCl_2 + 50H_2O = 1 + 0{\cdot}0001394t + 0{\cdot}000002892t^2$.
$CaCl_2 + 50H_2O\ \ 1 + 0{\cdot}0001925t + 0{\cdot}000002647t^2$.
$SrCl_2 + 50H_2O$ „ $1 + 0{\cdot}0002204t + 0{\cdot}000002542t^2$.
$BaCl_2 + 50H_2O$ „ $= 1 + 0{\cdot}0002393t + 0{\cdot}000002456t^2$.

Sodium and potassium bromides gave—

$NaBr + 50H_2O\ \ V_t = 1 + 0{\cdot}0001714t + 0{\cdot}0000033512t^2$.
$KBr + 50H_2O$ „ $= 1 + 0{\cdot}0001412t + 0{\cdot}0000035252t^2$.

The following general results were arrived at in the above and the former series :—

The change of volume with temperature, as expressed in the above equations, holds good only between 0° and 50°, when values are obtained agreeing within 0·00015 with the direct results of experiment; but for temperatures above 50°, differences are found exceeding the possible experimental errors. For such calculations, analogous equations must be used starting from 50°, at which temperature the volume is assumed = 1.

The change of volume with rise of temperature is best expressed by the first quotient dv/dt, the coefficient of dilatation. Up to 50° the coefficients are found to approach each other, the values varying from 0·000147 (for $LiNO_3 + 50H_2O$) to 0·000214 (for $NaNO_3 + 50H_2O$). For the solutions of chlorides, the differences of the single values are much larger at 0°, but with increase of temperature up to 50° they become smaller, not exceeding 12 per cent. The same is seen in the case of bromides.

On comparing the mean values of dilatation-coefficients at 40° and

50°, it is seen that they approach each other for salts of similar constitution:—

Temperature.	40°.	50°.
Nitrates	0·00045	0·00052
Chlorides	0·00040	0·00047
Bromides	0·00043	0·00050

The *atomic weights of elements forming the molecules*, and the molecules themselves at temperatures above 50°, are without influence on the dilatation, as seen, for example, from the fact that the dilatation of nitric acid is nearly identical with that of silver nitrate; the same is seen in the case of some of the chlorides, whereas in others the dilatation-coefficient increases with the atomic weight of the metal:—

$MgCl_2 + 50H_2O = 0·000429$
$CaCl_2 + 50H_2O = 0·000457$
$SrCl_2 + 50H_2O = 0·000474$
$BaCl_2 + 50H_2O = 0·000485$

The values for monad metals do not differ much from those of dyad metals.

The relative proportion of the molecules of anhydrous salt and water is of the greatest influence on the dilatation, but for solutions of 1 mol. of salt in 50 mols. of water at 50°, the dilatation is nearly the same in all cases. The proportion of the number of molecules of the hydrate existing at that temperature in solution to the number of molecules of the solvent, seems to be one and the same for the salts in question, but at lower temperatures, this proportion varies considerably for every salt, and the difference between the corresponding dilatation-coefficients is far more considerable, and varies with the temperature.

Mendeléeff (see Trans., 1888, 357, foot-note) regards solutions as compounds of different hydrates of salts with water, the hydrates existing in a state of formation and dissociation, and the author (Tschernay) regards Mendeléeff's hypothesis as a very probable explanation of the fact that the coefficient of dilatation varies with varying temperature for each salt in a different manner. B. B.

Vapour-density Estimation under Diminished Pressure. By C. SCHALL (*Ber.*, **22**, 140—146).—The principle on which the apparatus is constructed is as follows:—The pressure of an amount of air, let into the bulb and measured under ordinary conditions, is compared with the pressure of the vapour evolved in the latter. The capacity is thus found for the normal pressure and temperature. The apparatus is described with sketch (compare Abstr., 1887, 695 and 882). N. H. M.

Water of Crystallisation of the Alums. By W. MÜLLER-ERZBACH (*Ber.*, **21**, 3538—3540).—A reply to Lescœur and Maturin (this vol., p. 7).

Selective Chemical Affinity. By N. Beketoff (*J. Russ. Chem. Soc.*, 1888, **20**, 525—533).—Chemical affinity, since the time of Newton, has been regarded by some as a manifestation of universal gravitation or as an inclination of matter to aggregation; by others, as a peculiar power of affinity, analogous to magnetic or electrical attraction, since it is selective, or behaves differently with different particles of matter. The author regards affinity not as a peculiar force, but as a peculiar manifestation of energy. As a typical example, take a mixture of different halogens and of alkali metals. The result will be the formation of alkali haloïds, that is, compounds of the halogens with the alkali metals, accompanied by development of heat, and not a combination of the halogens or of the metals among themselves, which would take place without appreciable development of heat. Moreover, an apparent change of volume and loss of the original properties of the substances takes place in the first case, but would not do so in the second. This instance of aggregation is at first sight different from the phenomena of gravitation, cohesion or adhesion. An analogous case would occur if the motion of planets round the sun were arrested, when they would fall into the sun, with development of heat; but if their original motion could be restored to them, the former state might be re-established. Something analogous takes place in the case of phenomena of selective affinity. The atoms may be assumed as gifted with a store of energy, for example, in the form of vortex motions. This motion hinders their close approach or union, which would result in the formation of chemical compounds; it is a repulsive force acting against aggregation. In order to unite, the atoms must lose this motion partly or entirely, but the energy cannot be taken away, even at the temperature of absolute zero, as seen from the fact that the product of heat capacity c and absolute temperature T, that is Tc, is only a part of the heat set free on combination. The only thing that is capable of taking away or annihilating this motion is the action of an element of opposite properties: then chemical combination ensues. An analogous case occurs when two masses moving in opposite directions meet each other. The author assumes that atoms of different elements are gifted with motions, different in form, velocity, and quantity, and that these dynamical attributes are greatest for elements placed at opposite ends of periods when arranged according to the natural system as represented by the periodic law. Atoms of the same element may combine to form a molecule comparatively stable towards physical influences, but this stability vanishes when an element of opposite properties enters the sphere of motion. The two opposite motions neutralise one another, and a new, more stable system, that is, a chemical combination, is formed, with a loss of energy. According to this view, the phenomena of selective affinity become intelligible, and it is seen that chemical affinity is different from the usual forms of attraction between masses and particles.

If we do not assume the *hypothesis of opposite motions*, the masses and particles of bodies might be expected to show the same inclination for combining, so that the most stable aggregates would be formed from atoms and molecules of identical and homogeneous substances. It is true that combination of identical or like atoms takes place comparatively easily, but the compounds formed, chloride of bromine, for example, or alloys, show no *chemical* change in their original properties, and their stability is physical merely, and not chemical.

The author shows that the proposed hypothesis is in complete accordance with the thermal phenomena and with the change of volume accompanying chemical processes. The following tables, I and II, show for many others that a great contraction corresponds with, and, in the case of nearly related elements, is even proportional to, the development of heat.

TABLE I.

Compounds.	Contraction per cent.	Heat of formation.	Contraction per cent.	Heat of formation.	Contraction per cent.	Heat of formation.
	Cl.	Cl.	Br.	Br.	I.	I.
K........	48·4	105·6	38·0	95·3	24·0	80·0
Na.......	46·0	97·7	30·0	85·7	12·3	69·0
Li........	45·7	93·8	—	—	—	61·0
Ba.......	40·0	97·0	22·0	85·0	—	—
Ca.......	35·7	85·0	—	—	—	—
Pb.......	32·0	41·3	21·0	32·2	8·0	20·0
Ag.......	30·8	29·3	20·7	22·7	—	13·8

TABLE II.

Compounds.	Contraction per cent.	Heat of formation.
MgO...............	62·0	149·0
Li_2O...............	61·4	140·0
CuO...............	60·0	131·0
Na_2O..............	58·0	100·0
ZnO...............	47·0	85·0
PbO...............	31·0	55·0
BaO...............	40·3—47·7	124·0
Cu_2O..............	22·0	40·8

TABLE III.

Compounds.	Contraction per cent.	Heat of formation.
NaI + Cl = NaCl + I.....	23·5	28·7
KI + Cl = KCl + I.....	22·8	25·6
NaI + Br = NaBr + I.....	13·0	16·7
NaBr + Cl = NaCl + Br....	13·4	12·0
KBr + Cl = KCl + Br....	10·0	10·3
AgBr + Cl = AgCl + Br....	6·9	6·6

The same may be seen from Table III, representing phenomena of substitution. It would appear that the hypothesis of reciprocal annihilation of motion in chemical action is in accordance with the phenomena of contraction and of heat. But there is another cause on which the phenomena depend. The author showed, in 1859, that the distribution of the atoms of elements in a given system depends on the relative weight of the atoms acting on each other, and that the distribution proceeds in such a manner that smaller atoms combine with smaller, and larger atoms with larger ones. Such a distribution corresponds with the general inclination of matter to aggregation, and is accompanied by greater condensation and increased development of heat. This is apparent from the phenomena of double decomposition, but not in solutions, as the $\pm$ heat of dissolution obscures the phenomena. For, whereas, in solution, the "modulus" expressing the heat of substitution of one element by another is nearly constant (Favre and Silbermann), in the solid state this modulus changes from positive to negative values within wide limits. For example, when oxygen in oxides of alkali metals is displaced by chlorine, the heat developed decreases with decreasing weight of the metal, $\frac{K_2O}{2} + Cl = +57$; $\frac{Na_2O}{2} + Cl = 47{\cdot}5$; $\frac{Li_2O}{2} + Cl = 23{\cdot}2$. When oxygen is displaced by iodine there is at last a reversion of affinity, $\frac{K_2O}{2} + I = +32$; $\frac{Na_2O}{2} + I = +19$; $\frac{Li_2O}{2} + I = -10$; for in the case of lithium iodide the difference of atomic weights is very great, $\frac{Li = 7}{I = 127}$, and therefore the heat of formation of the oxide, $\frac{Li = 7}{O = 8} = 70$ Cal., is larger than that of the iodide. Lithium iodide is, therefore, easily decomposed by the oxygen of the air. A reversed action similar to that of oxygen and the halogens is seen in the case of hydrogen compounds; the formation of water, for instance, is accompanied by greater development of heat than that of hydrogen chloride, $H + \frac{O}{2} = 29$; $H + Cl = 22$; $\frac{H_2O}{2} + Cl = -7$. This difference is much larger for hydrogen bromide and iodide, the relation of the atomic weights $\frac{1}{80}, \frac{1}{127}$ being still more unfavourable for saturation than $\frac{1}{35{\cdot}5}$.

The influence of the relative weight of combining atoms or equivalents, in the case of different atomicity, is easily understood from the above point of view. The attraction of material particles increases with decreasing distance, and in the same way it increases as the acting masses become larger. Here we have another cause which promotes such a distribution; we can admit that the motions of atoms of nearly equal weight, if they are opposite in direction, will be most likely to completely neutralise each other. In the case of the formation of compounds with absorption of heat, the energy becomes greater, and the endothermic compounds formed will be less stable than the molecules of their simple constituents, so that under the influence of chemical or physical agents they will show an inclination to pass readily into more stable systems, in which the atoms possess a smaller store of energy. The physical stability of such compounds will depend mostly on the relative weight of the constituent atoms, that is, on the equal or nearly equal heat capacity. B. B.

Influence of Temperature on the Direction of Chemical Reactions. By A. POTILITZIN (*J. Russ. Chem. Soc.*, 1888, **20**, 503—506).—Claim of priority referring to Menschutkin's recent work, "Outlines of the Evolution of Chemical Views." B. B.

Formation of Amides from Ethereal Salts and Ammonia and the Reversal of the Reaction. By A. BONZ (*Zeit. physikal. Chem.*, **2**, 865—900).—The incomplete nature of the reactions for the formation of amides from ethereal salts and ammonia, led the author to suspect that the change was probably a reversible one. He found on experiment that this was the case, and that acid amides are, by the action of alcohol, partially converted into ethereal salt and ammonia. The two reactions were therefore further studied with a view of ascertaining the limits of each, and whether equilibrium exists between the two.

A large number of experiments were conducted which fully establish the reversible nature of both reactions, and show that the limits of each depend on molecular weight, temperature, and mass proportion. The higher the molecular weight of the ethereal salt, the less will be the quantity of amide formed and the greater will be the extent of the reverse reaction. Increase of temperature acts on the formation of the amide like increase of molecular weight, although at the same time the reaction is more rapid at high than at low temperatures. At high temperatures (above 100°), secondary reactions giving rise to the formation of amines also occur. H. C.

Dead Space in Chemical Reactions. By G. WATSON (*Chem. News*, **58**, 297).—The author attributes the dead space in chemical reactions observed by O. Liebreich (Abstr., 1888, 1242—1243) to the surface energy of the glass of the containing vessel. D. A. L.

Standard of Atomic Weights. By B. BRAUNER (*Chem. News*, **58**, 307—308).—The author points out how seriously the numbers representing the atomic weights are affected by the varying results obtained by different investigators for the ratio H : O, and suggests that instead of the atomic weights depending on this ratio, "the most difficult of all atomic ratios to determine accurately," it would be better to take O = 16, so as to make the atomic weights real Constants of Nature, and thus have to change these values only when a more exact determination replaces a less accurate predecessor.

D. A. L.

Apparatus for Determining the Reduction of the Freezing Point. By J. F. Eykman (*Zeit. physikal. Chem.*, **2**, 964—966).—A sketch of the apparatus, which is exceedingly simple, is given. It consists of a vessel of about 10 c.c. capacity, into which a small thermometer is so fitted as to act as a stopper. The whole can easily be weighed, and a stirrer is unnecessary as it can be taken in the hand and shaken. The details of a number of experiments with various plant substances in phenol show that it gives satisfactory results.

H. C.

Calculation of the Molecular Volumes of Benzene, Naphthalene, Anthracene, &c. By J. A. Groshans (*Rec. Trav. Chim.*, **7**, 263—267; compare this vol., p. 100).—For hydrocarbons containing two or three phenyl groups, 30 or 45 must be substituted for 15 in the formula $v_s = a - 15 + 2{\cdot}72$ B. For naphthalene, the value is 30, and for anthracene 45. If two substances belonging to the same series, fatty or aromatic, differ in their formulæ by 1 carbon-atom, their molecular volumes will differ by 14·72. H. C.

Lecture Experiments on Raoult's Law. By G. Ciamician (*Ber.*, **22**, 31—32).—The author describes, with the aid of a diagram, an apparatus suitable for lecture experiments on Raoult's law. It consists of an air-thermometer bent twice at right angles, the bulb of which, situated on the shorter limb, is placed in a large test-tube and encircled by a stirring-rod. The open and longer end dips into a beaker of coloured water and is provided with two bulbs, one near the extremity to prevent air being forced out of the thermometer, the other close to the bend serving to prevent the liquid from rushing back into the bulb. The solution is placed in the test-tube, the latter being surrounded by a beaker containing the cooling solution or freezing mixture. F. S. K.

Lecture Experiment: Volumetric Composition of certain Gaseous Compounds. By P. Hawkridge (*Chem. News*, **59**, 66—67).—The following arrangement serves for determining the composition of certain gases by heating with or by contact with a solid. A piece of wide glass tube is fitted into the tubulure of a 2-oz. retort by means of india-rubber tubing, the end of the tube inside the retort is plugged with asbestos, on this, sodium or any desired metal is packed, and a glass rod is fitted to the other end of the tube by means of india-rubber tubing. The retort is filled first with mercury, then with the gas to be examined, it is now stood upright with the end of the neck immersed in mercury. By pressing the rod, the metal is projected into the bulb of the retort, and may be heated; the contraction of the gas is measured by the rise of mercury in the neck of the retort.

D. A. L.

Blue Flame produced by Sodium Chloride in a Coal Fire. By N. Leonard (*Chem. News*, **59**, 15).—In connection with the blue flame produced when salt is thrown into a coal fire, the author points out that under similar circumstances the blue flame is produced equally well by potassium chloride, less readily by barium, calcium, and ammonium chlorides, also by chloroform, carbon tetrachloride, and ethylene dichloride, but that it is not produced by throwing sodium carbonate, phosphate, or sulphate into the fire, nor by dropping salt on red-hot platinum. These results support the view that the coloration is due to the chlorine of the salt. D. A. L.

Inorganic Chemistry.

Imperfect Combustion in Gaseous Explosions. By H. B. Dixon and H. W. Smith (*Chem. News*, **59**, 65—66).—The authors have observed that when mixtures of oxygen and hydrogen are exploded in a very long tube in proportions approximating to 2 vols. of the latter to 1 vol. of the former, an explosive residue always remains unburnt, even when the oxygen is in excess. In a number of experiments, the tube, after explosion, was filled with carbonic anhydride, until the internal pressure equalled that of the atmosphere, then a litre of gas was driven out of the other end of the tube, collected over soda and the unabsorbed gas analysed; the mean results of numerous analyses are given in the following table. It had been previously ascertained, that practically all the residual gas could be collected in the first litre expelled from the tube. The numbers under A are those obtained from the residue after the explosion of a mixture which contains a slight excess of hydrogen, whilst under B and C are given the mean results obtained from original mixtures containing excess of oxygen. The tube was 100 m. long, had a capacity of 8100 c.c., with a diameter of 9 mm. with an internal surface of 29,000 sq. cm.

	A.	B.	C.
Average residue..	150 c.c.	160 c.c.	220 c.c.
H..............	54·3 p. c.	29·5 p. c.	20·5 p. c.
CO..............		5·1 „	5·8 „
O..............	19·4 „	38·1 „	32·7 „
N..............	26·3 „	27·3 „	41·0 „

Other experiments show that the extent of surface of the vessel or tube employed does not exert any great influence on the explosion of the gases. Similar results were obtained in experiments with mixtures of carbon monoxide and oxygen. These results seem to confirm Mallard and Le Chatelier's observation, that the cooling in this method of combustion is more rapid than in ordinary combustion, and they also bear on Berthelot's theory of the mode of propagation of explosion waves. D. A. L.

Coefficients of Volatility for Aqueous Hydrochloric Acid. By R. B. Warder (*Amer. Chem. J.*, **10**, 458).—Expressing the strength of dilute hydrochloric acid by $H_2O + n$HCl, and the liquid which distils at any moment from such acid by $H_2O + v$HCl, the author tries to express the ratio existing between v and n by a constant factor as $v = 445n^3$ or $v = 3063n^4$, but as the values of v vary 10—30 per cent. with different conditions of boiling, no progress is made. H. B.

Rate of Decomposition by Heat of the Salts of the Halogen Oxy-acids and the Products obtained. By A. Potilitzin (*J. Russ. Chem. Soc.*, **20**, 1888, 541—570; compare Abstr., 1888, 219).—Lithium chlorate was prepared by the double decomposition of barium chlorate with lithium sulphate. It forms very hygroscopic needles of the formula $2LiClO_3 + H_2O$. It melts at about 50°, and the liquid, owing to superfusion, remains in that state at the ordinary temperature. On heating at 90° in a current of dry air, it becomes anhydrous, and then melts at 129°. On solidifying, two modifications separate, one in crystals and the other as a porcelain-like, white mass. The salt begins to decompose at 270°, but to a small extent only; at 323° the amount of decomposition varies from 0·19 to 0·63 per cent. in 20 minutes, or equals 2·85 per cent. in 3 hours 25 minutes. In order to study this decomposition, a weighed quantity of the dry salt was heated in a glass tube placed in a bath of Wood's alloy. The decomposition was as follows :—

Per cent.	17·10	34·08	37·10	36·54	41·11	41·60
Temp. ..	328°	338°	348°	358°	368°	383°
Time ...	7h. 20m.	8h. 40m.	8h. 20m.	3h. 30m.	5h. 50m.	2h. 30m.

The theoretical limit of total decomposition is 53·03 per cent., and the above rates of decomposition were calculated from a series of weighings after heating for 10 minutes at corresponding temperatures. It is seen that after some time, the amount of decomposition reaches its maximum, and then gradually decreases without reaching the theoretical limit. This maximum, moreover, is reached the sooner the higher temperature :—

Temperature	328°	338°	348°.	358°	368°	383°.
Maximum reached after........ .	5h. 40m.	2h. 20m.	1h. 20m.	40m.	10m.	<10m.
Limit of decomposition per cent..	—	—	37	—	40	41·6

The incomplete decomposition is due to the formation of some lithium perchlorate (by secondary reaction) which decomposes less easily than the chlorate (primary reaction) under the same conditions. The lithium perchlorate could be easily converted into the characteristic crystals of potassium perchlorate. The following equation represents the decomposition of lithium chlorate: $A\mathrm{LiClO_3} = m\mathrm{LiCl} + n\mathrm{LiClO_4} + p\mathrm{O}$. At the same time, some chlorine escapes, and some lithium oxide remains with the products of decomposition. In order to determine the amount of chloride and perchlorate formed in the different phases of the process, a weighed portion of the chlorate was heated as above, to 368°, weighed again, dissolved in water, and then in one part of the solution the chlorine of the chloride determined volumetrically with silver nitrate; in another part, the chlorine of the chlorate plus that of the chloride was determined in the same way, after evaporation to dryness with hydrochloric acid; the perchlorate is not acted on by the acid.

The result of a series of experiments is given in a table, and the theoretical facts deduced from it are the following:—The first period of the decomposition is represented by the equation: (*a*) $6LiClO_3 = 4LiCl + 2LiClO_4 + 5O_2$, whereas towards the end, the following reaction occurs: (*b*) $10LiClO_3 = 8LiCl + 2LiClO_4 + 11O_2$. It is seen from the numerical data, that the changes from the first to the second phase are not abrupt, but slow and continuous. The author shows in addition to this that lithium perchlorate is decomposed by heat into the chlorate and chloride, so that the reactions (*a* and *b*) are accompanied by a reversed reaction (*c*), $A LiClO_4 = n LiCl + m LiClO_3 + pO$. Both reactions are in contradiction to the principle of the maximum of work, and in fact the decomposition of lithium chlorate is not a simple one, representing a state of unstable equilibrium between the chlorate, perchlorate, chloride, and oxygen, the direction of the change depending on the temperature and the relative quantity of the substances present.

An analogous set of experiments was carried on with lithium perchlorate. This was prepared by dissolving pure lithium carbonate in perchloric acid, and purifying the salt by fractional precipitation with lithium carbonate, and treatment with absolute alcohol and recrystallisation. It forms either short prisms belonging to the hexagonal system or thin needles; it does not deliquesce on exposure to the air. The crystals are hexagonal-hemihedric with the forms R_1—R (which in an equilibrium form the pyramid P) ∞P and ∞P2. Axial ratio: $a : c = 1 : 0{\cdot}7039$. Optically monaxial. Bifraction negative. (A. Lagorio.) The crystals which have the composition $LiClO_4 + 3H_2O$ seem to be isomorphous with those of barium perchlorate; 2 mols. of H_2O are lost at 98—100°, and the third at 130—150°, the weight remaining constant up to 300°. The hydrated salt fuses at 95°, the anhydrous at 236°. It absorbs moisture, but does not deliquesce. At 380°, decomposition begins and increases rapidly with rise of temperature; at 415° the loss of oxygen is equal to 22—23 per cent. (theoretical limit 60·09 per cent.), this being the maximum. At higher temperatures, the amount of decomposition decreases. The greatest velocity of decomposition is more removed from the initial decomposition than in the case of the chlorate. The rate of decomposition is greatest at a moment when, at a certain temperature, the relative proportion of the chlorate and perchlorate which are mutually converted, is the greatest. This temperature lies about 368° when the mixture has the composition $3LiClO_3 + 2LiCl + LiClO_4$.

The phases of the decomposition of lithium chlorate and perchlorate, like those of barium bromate, cannot be foreseen and explained from the point of view of the "principle of maximum work," but are easily explained by the following rule of unstable equilibrium as shown by the author in 1880. In every case of chemical transformation, the equilibrium of the system of bodies depends on their atomic weights, their relative quantities (masses), and the store of internal and external energy. It is shown that the different phases of the reactions studied are in complete accordance with this law.

B. B.

Molecular Weight of Sulphur. By H. Biltz (*Zeit. physikal. Chem.*, 2, 920—947).—The author describes the details of his work on the molecular weight of sulphur, the results of which have been already given (Abstr., 1888, 1027).

Hydrazine. By T. Curtius and R. Jay (*J. pr. Chem.* [2], **39**, 27—58; compare Abstr., 1887, 715).—Hydrazine sulphate is best obtained when triazoacetic acid (250 grams in 2 litres of water, this vol., p. 369) is warmed with sulphuric acid (300 grams) until all effervescence ceases; the sulphate crystallises out on cooling. More may be extracted from the mother-liquor by shaking with small quantities of benzaldehyde, thus converting the hydrazine into benzalazine (see p. 393), which separates out; after recrystallisation this is decomposed with sulphuric acid, whereby hydrazine sulphate and benzaldehyde are reformed; the latter is then distilled off. The yield is 90 per cent. of that calculated. The same process will serve to extract the hydrazine contained in the mother-liquor from the preparation of triazoacetic acid (this vol., p. 369), and from the solution resulting from the reduction of ethyl diazoacetate in the presence of either acid or alkali.

The decomposition of triazoacetic acid by mineral acids is expressed by the equation $C_3H_3N_6(COOH)_3 + 6H_2O = 3N_2H_4 + 3C_2O_4H_2$, but during the reaction the oxalic acid splits up more or less completely into formic acid and carbonic anhydride. The authors observe that ammonium formate melts between 114° and 116°.

Hydrazine dihydrochloride (Abstr., 1887, 715) melts at 198° to a clear glass, evolving hydrogen chloride, and being converted into the *monohydrochloride* N_2H_4,HCl, which separates from hot absolute alcohol in long, white needles melting at 89°; it is decomposed at 240° into ammonium chloride, nitrogen, and water, and is very soluble in water. These hydrochlorides reduce platinic chloride in acid solution with evolution of nitrogen, no platinochloride being formed. *Hydrazine formate*, $N_2H_4,2H{\cdot}COOH$, is obtained by heating triazoacetic acid with water; it crystallises in rectangular tables melting at 128° with evolution of gas; the *carbonate*, *acetate*, *oxalate*, and *nitrate* have also been obtained.

Hydrazine itself is still unknown (compare Abstr., 1887, 715); its *hydrate*, N_2H_4,H_2O, is obtained, instead of the free base, when the hydrochloride is heated with caustic lime in a silver retort, and the resulting vapour passed through a silver tube containing caustic lime, and likewise heated: it is not dehydrated by barium oxide. It is a fuming, highly refractive, nearly odourless liquid, boiling at 119° unchanged; when hot it corrodes glass and destroys cork and rubber; it tastes alkaline and burns the tongue, and has most remarkable reducing powers. Some of its reactions with metallic salts are given. It is nearly destitute of odour. (For the remainder of this paper see p. 393.)

A. G. B.

Nitric Anhydride. By L. MEYER (*Ber.*, **22**, 23—24).—When phosphoric anhydride is mixed with almost anhydrous nitric acid, no heat is generated as stated by Weber (*J. pr. Chem.* [2], **6**, 342); the hissing noise and the evolution of brown fumes only take place when the acid contains more water than that obtained by distilling slowly with sulphuric acid.

Nitric anhydride has a more violent action on benzene than nitric acid, but the nitration does not proceed further than when the acid is employed. At 55° only dinitrobenzene is formed; trinitrobenzene is not produced until the dinitro-compound is heated with nitric anhydride and concentrated sulphuric acid at 160°. F. S. K.

Hypophosphoric Acid and its Salts. By P. DRAWE (*Ber.*, **21**, 3401—3404).—Hydrogen sodium hypophosphate is best prepared by allowing phosphorus to oxidise slowly in moist air as described by Salzer, and collecting the oxidation products in a 25 per cent. solution of sodium acetate. When a solution of nickel sulphate is added to a solution of hydrogen sodium hypophosphate in presence of sodium acetate, two salts are obtained, one of which, $Ni_2P_2O_6 + 12H_2O$, crystallises in prisms, the other, $NiNa_2P_2O_6 + 12H_2O$, in hexagonal plates. When the addition of sodium acetate is omitted, the prismatic crystals alone are formed, but when a solution of nickel sulphate is added to a solution of sodium hypophosphate both salts are produced. *Nickel hypophosphate*, $Ni_2P_2O_6 + 12H_2O$, is best prepared by adding a warm, dilute solution of sodium hypophosphate to excess of a warm solution of nickel sulphate, with constant stirring, and drying the precipitate in the air. *Nickel sodium hypophosphate*, $NiNa_2P_2O_6 + 12H_2O$, is obtained in the pure state by gradually adding a very dilute and well-cooled solution of nickel sulphate to excess of a very dilute and well-cooled solution of sodium hypophosphate, and drying the precipitate in the air.

The following salts, $Co_2P_2O_6 + 8H_2O$; $CoNa_2P_2O_6 + 1\frac{1}{2}H_2O$; $Cd_2P_2O_6 + 2H_2O$; $CdNa_2P_2O_6 + 6H_2O$; $Cu_2P_2O_6 + 6H_2O$; and $Zn_2P_2O_6 + 2H_2O$, were prepared as described above in the case of the corresponding nickel compounds. The salts are soluble in dilute acids, but almost insoluble in water; the double salts are decomposed by water. Some of the salts lose part of their water when heated at 110°, and their weight becomes constant, others are oxidised or decomposed. Cadmium hypophosphate is converted into the phosphide when ignited in the air, whereas nickel and cobalt hypophosphates are oxidised and become constant in weight, but the increase is less than what would correspond to a conversion into pyrophosphate.

F. S. K.

Arsenic in Glass and in Alkali Hydroxides. By J. MARSHALL and C. S. POTTS (*Amer. Chem. J.*, **10**, 425—430).—The amount of arsenious oxide in glass laboratory apparatus of American and German manufacture was found to vary from 0·095 to 0·446 per cent. All the samples of soda examined contained amounts of arsenic trioxide varying from 0·0028 to 0·0848 per cent.; a sample prepared by the Solvay process, however was free from arsenic. A 10 per cent. solution of soda readily dissolves arsenic from arsenical glass, but ammonia, and hydrochloric and sulphuric acids are without effect. Samples of potash were found to be free from arsenic, and sodium carbonate, although sometimes contaminated, was easily purified by recrystallisation. H. B.

Silicon and Boron. By L. GATTERMANN (*Ber.*, **22**, 186—197).—When quartz sand is heated with magnesium powder in a test-tube, a reaction takes place, and the whole glows intensely; if precipitated silica is used the reaction is very violent. Magnesium silicide is readily prepared by heating finely powdered, dry sand with powdered magnesium (1·5 part); the product is a bluish, half-fused substance which, when added to strong hydrochloric acid, at once gives rise to an evolution of silicon hydride. The residue has all the properties of the lower oxide of silicon; it burns when heated in air, reduces silver solutions, and reacts with alkalis with evolution of hydrogen. The experiments are very suitable for lecture experiments.

Silicon is best prepared by heating dry, finely powdered sand (40 grams) with magnesium (10 grams) in a not too thin test-tube; the whole tube is first heated moderately, and then a small portion is strongly heated, beginning at the lower end and continuing upwards. The product is greyish-black. The fragments of the test-tube, after the substance has been taken out, should be treated with acid, as the adherent substance will decompose in the moist air and evolve silicon hydride. Silicon is obtained by heating the substance in a closed crucible with zinc; on dissolving out the zinc, it is obtained in steel-blue needles.

Silicon tetrachloride is very readily prepared by gently heating the reduction-product in a tube in a stream of dry chlorine, and collecting in a receiver cooled with ice and salt. The product, which is greenish from dissolved chlorine, is purified by means of mercury. The yield is very good.

Silicon tetrabromide is prepared in a similar manner, but the receiver is merely cooled with water. The product is purified by distillation, and finally by shaking with mercury, and again distilling. The yield is not so good as in the case of the chloride, and the compound is more easily prepared from silicon and hydrogen bromide.

Silicon tetriodide is obtained by heating the reduction-product in a stream of dry carbonic anhydride and iodine vapour; a higher temperature has to be used than in the case of the chloride. The product is dissolved in carbon bisulphide, shaken with mercury until colourless, and the carbon bisulphide evaporated at a low temperature in a stream of carbonic anhydride. It is thus obtained in splendid, colourless crystals.

Silicon chloroform is readily prepared as follows:—The reduction-product is first freed from magnesia by keeping the powdered substance for some hours in contact with dilute hydrochloric acid (1 : 2); it is then washed well with water, dried, and heated in a stream of dry hydrogen chloride. It is preferable to first pass dry hydrogen over the heated substance to remove the last traces of water. The product is distilled in a distilling flask heated by means of a small vessel containing water at 90° which can be readily controlled. When a few drops of the compound are volatilised in a warm cylinder, and a slightly heated glass rod held at the opening, the substance ignites and explodes.

Silicoformic acid is easily obtained by connecting the receiver used in the preparation of silicon chloroform with a vessel containing ice-water. The uncondensed silicon chloroform on coming into contact with the water is decomposed, and flakes of silicoformic acid separate. It is filtered, washed with water, then with absolute alcohol, and finally with ether.

Silicon bromoform is prepared in a manner similar to silicon chloroform; a large amount of silicon tetrabromide is also obtained, so that it is better to prepare the tetrabromide by this method than by the method previously described. Silicon bromoform is spontaneously inflammable in the air, burning with a flame like that of zinc ethyl. It boils at 115—117°, sp. gr. = 2·7.

Silicon tetrachloride reacts with ammonia, yielding the compound $Si(NH)_2$ or $N\colon Si\cdot NH_2$; this is a white substance which does not melt. When silicon chloroform is treated with chlorobenzene and sodium, silicon tetraphenyl (m. p. 231°) is formed.

Boron is prepared by heating a mixture of magnesium (1 part) and dry borax (2 parts), covered with a layer of borax, to keep out the air, in a Hessian crucible for a short time. The product is powdered, extracted, first with hot water, and then with boiling hydrochloric acid. It is then washed, dried, and heated with aluminium in a crucible, when splendid hexagonal plates are obtained.

Boron trichloride is readily obtained by slightly heating the crude dried boron in chlorine. The greenish-yellow distillate is cooled in a freezing mixture, and shaken with mercury until colourless. 15 grams of the chloride were obtained when 8 grams of magnesium were used.

The author intends preparing aromatic derivatives of boron.

Lime, alumina, ferric oxide, chromic oxide, titanic and vanadic acids, &c., are also reduced by magnesium. N. H. M.

Graphite from Various Metals. By H. N. Warren (*Chem. News*, **59**, 29).—Cast iron, nickel, cobalt, ferromanganese, manganese, and chromium when treated with dilute acid leave scales of graphite differing in size, appearance, and combustibility in each case; but when some of the manganese graphite is added to molten iron, it is converted into the iron variety. D. A. L.

Decomposition of Potassium Chlorate in Contact with Metallic Oxides. By W. R. Hodgkinson and F. K. S. Lowndes (*Chem. News*, **58**, 309; **59**, 63—64).—When finely divided manganese dioxide is dropped into fused potassium chlorate, a sudden evolution of oxygen and chlorine ensues, the quantity of the latter gas depending on the fineness of the powdered oxide, at the same time some of the manganese enters into combination with the potassium. Oxides of cobalt, lead, iron, mercury, uranium, tungsten, molybdenum, and vanadium behave in a similar manner, the more acid oxides being most energetic, especially as regards the evolution of chlorine and formation of a potassium salt of the oxide. Platinum-black causes a temporary increase in the evolution of oxygen from fused potassium chlorate, but the action is purely mechanical.

Zinc, magnesium, bismuth, antimony, copper, and tin oxides, however, produce little or no effect when added to fused potassium chlorate. From a series of quantitative experiments, the authors are inclined to conclude that under the above circumstances the manganese dioxide suffers alternate reduction and re-oxidation, but the re-oxidation is rarely complete. In a similar way, Ag_2O is reduced to Ag and PbO_2 to Pb_3O_4. In other experiments, they show that the evolution of chlorine is due to the potassium forming manganates, uranates, vanadates, &c., as the case may be. Potassium chlorate is also decomposed by many salts, especially those of ammonia. D. A. L.

Extraction of Lithium from its Minerals. (*Pharm. J. Trans.* [3], **19**, 6.)—The method formerly in use for separating lithium from the other alkalis was based on the slight solubility of its carbonate. Schering now employs the following process for extracting lithium from *lepidolite* on the large scale. The finely ground mineral is digested with concentrated sulphuric acid, and the product is calcined and lixiviated with water. Potassium sulphate, sufficient to convert all the aluminium present into alum, is added, and after evaporation the alum which separates is removed, any portion remaining being afterwards decomposed by the addition of milk of lime. The filtrates are mixed with barium chloride, whereby all the bases are converted into chlorides. The whole is then evaporated to dryness, and extracted with absolute alcohol, which dissolves the calcium and lithium chlorides. The calcium chloride in the residue left on distilling off the alcohol is decomposed by ammonium oxalate; the filtrate is evaporated to dryness, and again extracted with absolute alcohol, which after evaporation leaves pure lithium chloride.

R. R.

Solubility of Various Forms of Calcium Carbonate in Sea-water. By R. IRVINE and G. YOUNG (*Proc. Roy. Soc. Edin.*, **127**, 316—320).—The investigations were undertaken with the view of throwing additional light on Murray's theory as to the formation of coral island lagoons. The authors found a marked difference in the solubility of various corals, the porous kind being most easily dissolved by sea-water. This is due to the fact that porous corals present a larger surface to the action of sea-water, and also that the carbonate appears to be in a different molecular condition. Precipitated amorphous calcium carbonate dissolves in 1600 parts of sea-water, whilst of the same precipitate, when it has changed from the amorphous to the crystalline condition, 1 part requires 8000 of sea-water to dissolve it. Moreover, porous corals contain a large proportion of organic matter, which on oxidising produces carbonic anhydride, and so increases the solvent action of the water. The solution thus formed precipitates crystallised calcium carbonate, and this precipitation may be due either to loss of carbonic anhydride or to the formation of ammoniacal salts, which reduce the solubility. Once the crystalline form is produced, its greater insolubility protects it from further solution, and the protective influence of mud and sand and seaweed growth must also be considered. The action of sea-water on hard and soft corals is shown below.

Materials.	Temperature.	Exposure.	Average amount of $CaCO_3$ taken up.
	C.°	hours.	grams.
Dead corals, porites	27	12	0·395
Coral sand	27	12	0·032
Harbour mud (Bermuda)	27	12	0·041
Isophyllia dipsacea (Dana), Bermuda	—	—	0·041
Millepora ramosa (Pallas)	—	—	0·036
Madrepora asperosa (Dana), Mactan Isl., Zebu	—	—	0·073
Montipora foliosa (Pallas), Amboyna	—	—	0·043
Gomastræa multilobata (Quelch), Amboyna	10	—	0·073
Porites clavaria (Lamk), Bermuda	10	—	0·093

The effect of the presence of organic matter appears in the figures given below.

	Temp.	Hours.	Gram.
Weathered oyster shells	10° C.	12	0·331
Mussels allowed to rot in sea-water 7 days	17	168	0·384
Lobsters allowed to rot in sea-water 3 weeks	10	504	1·062
Shrimps allowed to rot in sea-water 3 weeks	—	504	1·047
Schizopoda allowed to rot in sea-water 3 weeks	—	504	0·782
a. Amorphous $CaCO_3$ (freshly prepared)	—	—	0·649
b. " " "	−1·66	—	0·610
Crystallised $CaCO_3$	10	12	0·123
Melobesia, Kilbrennan Sound, Scotland	10	12	0·089

In *a* and *b*, the $CaCO_3$ was added as long as it dissolved.

E. W. P.

Solubility of Strontium Nitrate in Alcohol. By J. R. HILL. (*Pharm. J. Trans.* [3], **19**, 420).—One part of strontium nitrate dissolves in 4189 parts of absolute alcohol, and in 199·87 parts of rectified spirit at 15·5°.

R. R.

Action of Ammonia on Metallic Magnesium. By H. N. WARREN (*Chem. News*, **58**, 297—298).—When magnesium is exposed to ammonia at a temperature below a red heat, although undergoing no apparent change, it becomes less fusible, and burns when ignited with violent decrepitations. At a dull red heat, the metal becomes yellow, with golden lustre; whilst at full redness it is converted into an orange-yellow powder, which evolves ammonia when its acidified solution is treated with sodium hydroxide. D. A. L.

Action of Hydrogen Sulphide on Zinc Sulphate. By H. Baubigny (*Compt. rend.*, **107**, 1148—1150).—A neutral solution of zinc sulphate, containing not more than 0·3 gram of salt in 100 c.c., is completely precipitated by hydrogen sulphide in the cold after several hours. With twice the quantity of zinc sulphate in the same volume of liquid, precipitation is less perfect, 0·004—0·006 gram remaining in solution. After three days, however, only 0·001 gram remained unprecipitated.

If the solution of zinc sulphate contains free acid, the phenomena are similar to those observed with nickel and cobalt. With 0·3 gram of salt in 100 c.c., the quantity of free acid required to prevent precipitation is 30 times the amount of combined acid in the salt. At a higher temperature, and a correspondingly higher tension of the hydrogen sulphide, decomposition proceeds further, and at 100° the quantity of free acid required is 90 to 100 times the quantity of combined acid. The more concentrated the solution, the smaller the quantity of free acid that must be added for a given weight of zinc salt in order to prevent precipitation. The decomposition is a function, not only of the ratio of free acid to water, but also of the ratio of free acid to the metal present in the form of a salt, just as in the cases of nickel and cobalt. C. H. B.

Mixed Double Sulphates of the Copper-magnesium Group. By Prafulla Chandra Ray (*Proc. Roy. Soc. Edin.*, **127**, 267—283). The accounts given of the constitution of these salts being conflicting, a large number were prepared and analysed. Of the mass of details of which this paper consists, it is impossible to make an abstract. It must suffice to say that "double-double" sulphates of definite composition do exist, and that the chemical affinity which determines the formation of such compounds is not indeed very powerful, but its influence is unmistakable if proper care is taken to avoid conditions under which it is necessarily obscured. The author believes that Aston and Pickering are completely mistaken in their views of these salts, and that their error is due to their methods of working, which brought about the formation of heterogeneous deposits. E. W. P.

Action of Sodium Hydroxide on Mercurous Salts. By C. Barfoed (*J. pr. Chem.* [2], **38**, 441—472).—The author has investigated the composition of the precipitate produced by the action of sodium hydroxide on mercurous salts, by treating it with gold chloride. He concludes that it is not, as previously believed, a mixture of mercury and mercuric oxide, but a mixture of mercurous oxide, mercury, and mercuric oxide in varying proportions; it sometimes contains as much as 81 per cent. of mercurous oxide. The mercurous oxide is oxidised by the air at the ordinary temperature both in the light and in the dark. In a limited volume of air, the precipitate retains its dark colour, but otherwise it becomes yellow as the mercury evaporates. At 100° these changes are more rapid, and there is less yellow oxide left, because a part only of the mercurous oxide is oxidised, the rest being split up. The finely divided mercury in the precipitate undergoes no oxidation in the air at the ordinary temperature, and in a small space much less of the mercury evaporates than would be expected from its accepted vapour-tension.

The reduction of gold chloride by mercury vapour forms a very delicate test, and occurs even at $-8°$. A. G. B.

Ammoniacal Mercury Compounds. By C. RAMMELSBERG (*J. pr. Chem.* [2], **38**, 558—569).—The author regards the pale-yellow product of the action of ammonia on mercuric oxide at the ordinary temperature, as a hydrate of mercurammonium hydroxide, $NHg_2{\cdot}OH,H_2O$, for it loses 4·1 per cent. of water over strong sulphuric acid. Millon's base is obtained when the pale-yellow compound is treated with either hot or cold aqueous ammonia; Millon gave it the formula $2HgO,NH_3,H_2O$, and Gerresheim (Abstr., 1879, 438) the formula $2(2HgO,NH_3),H_2O$, but the author's analyses show that it is $3(2HgO,NH_3) + 2H_2O$. By treating either of these compounds with dilute hydrochloric acid, the insoluble pale-yellow chloride which Kane formulates as Hg_2OClNH_2 is obtained; it loses water at 200°, and is the hydrate of mercurammonium chloride, NHg_2Cl,H_2O.

True "white precipitate" is infusible, but the officinal preparation, made by precipitating ammoniacal mercuric chloride by an alkaline carbonate, is fusible. The latter can be obtained from the former by boiling it with ammonium chloride; moreover, amorphous mercuric oxide at once yields the fusible precipitate when boiled with ammonium chloride solution; again, when the infusible precipitate is boiled with alkali it loses $\frac{1}{2}$ of its nitrogen as ammonia, whilst the fusible precipitate loses $\frac{3}{4}$ of its nitrogen as ammonia under the same circumstances. It would thus seem that they are both double compounds of ammonium chloride with mercurammonium chloride, the infusible being NHg_2Cl,NH_4Cl, and the fusible, $NHg_2Cl,3NH_4Cl$.

The author has obtained a whole series of mercurammonium salts by the direct action of acids on Millon's base. Of these the sulphate, nitrate, carbonate, phosphate, bromate, iodate, and periodate are described. A. G. B.

Action of Concentrated Sulphuric Acid on Solutions of Iron and Aluminium Sulphates. By F. A. EREMIN (*J. Russ. Chem. Soc.*, 1888, **20**, 468—477).—The author finds that the addition of sulphuric acid to a solution of aluminium sulphate throws down the salt, but as ferrous sulphate, if present, is also thrown down along with it, both salts were investigated in this respect. For this purpose the lower end of a separating funnel was plugged with glass-wool, a known volume of ferrous sulphate solution poured in, and then concentrated sulphuric acid of 66° B. was added from a burette. After 24 hours, the liquid was drawn off from the crystals formed and the amount of iron present in the solution determined volumetrically. This result was corrected for the amount of ferrous sulphate in the liquid adhering to the walls of the vessel employed, a determination having been previously made for that purpose. The first series of experiments was made with a concentrated solution containing 21 grams of $FeSO_4,7H_2O$ in 50 c.c., and it was found that the largest quantity of salt, 99·18 per cent., is precipitated when the solution is mixed with an equal volume of sulphuric acid, and that the percentage of salt precipitated is less whether the proportion of acid is greater or less than this. By using ferrous sulphate solutions of various degrees of concentration, the author finds that the amount of salt precipitated increases with increasing concentration of its solution, the volume of sulphuric acid added remaining constant. As regards the composition of the precipitate, it corresponds with the formula $FeSO_4,H_2O$, as long as for 5 c.c. of the solution, 5. 10, or 15 c.c. of sulphuric acid is added. When, however, 20 c.c. is added slowly, a mixture of monohydrated sulphate with a greenish-white, crystalline substance is precipitated, but the latter alone is formed if the sulphuric acid is added at once. These crystals have a brilliant lustre and are highly iridescent; their formula is $FeSO_4,5H_2SO_4,5H_2O$, but they are very unstable. At 95—97° they are decomposed as follows: $FeSO_4,5H_2SO_4,5H_2O = FeSO_4,H_2O + 5H_2SO_4,4H_2O$.

Chemically pure aluminium sulphate, containing no iron, was dissolved in water and its solution treated with sulphuric acid in precisely the same manner, but a very different result was obtained. Scarcely any precipitate is produced on adding an equal volume of sulphuric acid to a nearly concentrated solution of the aluminium salt, and the addition of two volumes of sulphuric acid produces no precipitate at all. But smaller quantities of sulphuric acid, which are without action on ferrous sulphate, give an abundant precipitate with the aluminium salt, so that the maximum precipitate is obtained on adding 1·5 c.c. of H_2SO_4 to 5 c.c. of aluminium sulphate solution. The precipitate thrown down on mixing equal volumes of the aluminium sulphate solution and sulphuric acid has the composition $Al_2(SO_4)_3,2H_2SO_4,16H_2O$; with 5 c.c. of the solution and 0·3 c.c. of sulphuric acid, the precipitate has the formula $Al_2(SO_4)_3,22H_2O$. The different behaviour of ferrous and aluminium sulphates towards sulphuric acid cannot be used, however, for their separation or for the preparation of pure aluminium sulphate, because some iron is always carried down mechanically with the latter. The author proposes to investigate the sulphates of the metals of the Third Group from the same point of view. B. B.

Solution for Depositing Metallic Cobalt. By H. N. WARREN (*Chem. News*, **59**, 64).—A concentrated solution of Rochelle salt is added to a solution of cobalt chloride until the precipitate first formed is redissolved; from this solution, the metal is readily deposited on any desired object attached to the negative electrode of a single cell battery. Nickel may be deposited in a similar manner, and when the solution contains nickel as well as cobalt, both metals are deposited in equal proportions and the deposit is darker and more durable than when cobalt alone is used. Zinc and several other metals may be deposited in a similar manner. D. A. L.

Nickel and Cobalt. By G. KRÜSS and F. W. SCHMIDT (*Ber.*, **22**, 11—15).—In the course of experiments which were commenced with the object of determining the atomic weights of nickel and cobalt, it was found that it was impossible to precipitate an equivalent quantity of pure gold from a neutral solution of auric chloride by means of metallic nickel or cobalt, because small quantities of these metals are again precipitated from the solutions of the chlorides which are produced. The precipitated gold was therefore washed, dried, ignited, and weighed, and then dissolved in aqua regia and precipitated with sulphurous acid. The metal thus purified weighed considerably less than the original precipitate, and although this difference was taken into account the results of various experiments were very discordant. In washing the gold precipitated by sulphurous acid from a solution of the powder which had originally been precipitated by cobalt, it was noticed that the filtrate gradually lost the red colour due to cobalt chloride and turned faintly green; on evaporating this portion of the washings, the slight residue which was obtained dissolved in warm, concentrated hydrochloric acid with a green coloration, but the solution became almost colourless on cooling. The same phenomenon was observed in washing the gold which had been precipitated by sulphurous acid from solutions of the metal obtained in similar experiments with nickel, but the quantity of the new chloride obtained was extremely small.

Nickel sulphide, prepared from the ordinary sulphate, was repeatedly treated with ammonium sulphide until the latter was no longer coloured brown; a bright-yellow residue was obtained and the relative quantity of the new substance present in this residue was far more than in the original sulphide. The chloride of this substance was also obtained from the mother-liquors of solutions containing equivalent quantities of mercuric chloride and nickel or cobaltous chloride, and by several other methods.

The pure oxide of this metal was obtained by making use of the fact that it is soluble in melted alkalis, nickel and cobalt oxides being insoluble.

Hydrogen sulphide produces no precipitate in acid solutions, but ammonium sulphide gives a blackish precipitate in neutral solutions of the chloride. Ammonia produces a white, very voluminous, flocculent precipitate in neutral solutions, and the precipitate is insoluble in excess of the reagent; potash also precipitates a white hydroxide insoluble in excess. When the oxide is moistened with cobalt solution, and heated, it becomes slightly brown; after having been strongly heated alone for a long time it is readily and completely soluble in cold, concentrated hydrochloric acid. Strongly acid solutions of the chloride have a peculiar greenish-yellow colour, but in the dry state, and when free from acid, the salt is white and dissolves in water, forming a colourless solution. When the vapour of hydrochloric acid is blown on to the white chloride, it turns greenish and then dissolves in water, forming a coloured solution. The oxide does not lose weight when heated in an atmosphere of hydrogen.

The metal can be obtained by the electrolysis of an aqueous solution of the chloride, or by heating the dry chloride in a stream of hydrogen.

It is black, but brownish-black in thin layers; it is readily soluble in acids when obtained by electrolysis in the cold, but when strongly heated in a stream of hydrogen it becomes much more sparingly soluble. F. S. K.

Interaction of Chromic Acid and Hydrogen Peroxide. By BERTHELOT (*Compt. rend.*, **108**, 24—31).—The blue compound to which Moissan (Abstr., 1884, 20) ascribes the formula CrO_3,H_2O_2, more probably has the composition $2HCrO_4,H_2O_2$. Both formulæ represent the same amount of available oxygen. The blue colour of the compound recalls the colour of permanganic acid, and the fact that it can be formed even in very dilute solutions distinguishes it from the ordinary compounds of hydrogen peroxide with acids, alkalis, &c.

When hydrogen peroxide reacts with permanganic acid, the action is reciprocal, and the volume of oxygen evolved is the same whether the peroxide is added to the permanganic acid, or *vice versâ*, a fact which indicates the formation of an intermediate compound. This is colourless and stable at a very low temperature. It probably has the composition H_2O_3, and decomposes into water and oxygen if the temperature rises.

With hydrogen peroxide and chromic acid, the phenomena are not quite similar, and the result varies with the mode of admixture, the temperature, and the concentration. When a very dilute solution of potassium dichromate acidified with hydrochloric acid is mixed with hydrogen peroxide, the ratio between the oxygen lost by the dichromate and that lost by the peroxide is 1 : 1·1, and the result is the same, whether the liquids are mixed gradually or rapidly. The difference is due to the intermediate formation of perchromic acid, and almost disappears in more dilute solutions.

If, on the other hand, with the same degree of concentration, the dichromate solution is added to the peroxide, the reaction takes place very slowly, and the end-point is very difficult to determine. The ratio between the oxygen evolved from the dichromate and that evolved from the peroxide is 1 : 1·52—1·63. With hydrogen peroxide containing barium chloride, the ratio obtained was 1 : 1·6. The formation of the intermediate compound could not, however, be detected in the calorimeter, the change taking place too rapidly. It is evident that the action of the peroxide on the chromic acid is not reciprocal, and it follows that in making titrations with these solutions (this vol., p. 311), the manner in which the liquids are mixed will influence the result.

The action of excess of chromic acid on hydrogen peroxide develops +45·6 Cals. for CrO_3. In presence of excess of the peroxide, the stability of the perchromic acid is greater, owing to the formation of the blue compound. The first stage of the reaction is represented by the equation $2CrO_3 + H_2O_2 = 2HCrO_4$, and the perchromic acid then interacts with a further quantity of the peroxide. Under the conditions described above, the reaction $2HCrO_4 + 4H_2O_2 + 6HCl = Cr_2Cl_6$ dil. $+ 4O_2 + 8H_2O$ develops +67·2 × 2. According to this

When brown ruthenic chloride is treated with so-called hyponitric acid, it is gradually converted into a non-crystallisable, violet-red liquid, which when mixed with alkaline chlorides yields the compounds just referred to. The reaction takes place only at a temperature at which the hyponitrous acid splits up into nitric acid and nitric oxide, and as a matter of fact the same product is obtained if ruthenic chloride is heated in nitric oxide. The salts are readily obtained by adding an alkaline nitrite to a warm solution of ruthenic chloride in hydrochloric acid.

If a mixture of ruthenium with potassium or sodium chloride is heated in chlorine gas, no rutheniochlorides are formed, and ruthenic chloride is the only product. It follows from these results that no true rutheniochlorides have yet been obtained, the salts described as such being really nitrosochlorides. Potassium chlorate, which removes all the metal from ruthenic chloride in the form of peroxide, has no action on the nitrosochlorides.

From analyses of these and other ruthenium compounds, the author is led to the conclusion that the atomic weight of ruthenium is 101·5. Debray's determination of the sp. gr. of gaseous ruthenium peroxide indicated that the atomic weight was less than 102. No details of the estimations are given. C. H. B.

Mineralogical Chemistry.

Fossil Resins from the Coal Measures. By W. I. Macadam (*Chem. News*, 59, 1—2).—The author has examined two samples of brown, resinous scales found in coals from the neighbourhood of Kilmarnock, and two samples obtained from the Chemise seam of the Methil district. These were treated first with ether, then with chloroform, and the respective resins analysed with the following results:—

	Kilmarnock coal, soluble in		Chemise seam coal, soluble in	
	Ether.	Chloroform.	Ether.	Chloroform.
Carbon	84·28	74·28	57·50	66·70
Hydrogen	9·36	6·52	7·53	7·32
Oxygen	6·36	19·20	34·97	25·98

The composition of the Kilmarnock resins approaches that of schlanite and anthracoxenite respectively. Attention is drawn to the fact that the resin soluble in ether is partially volatile much below 100°, probably due to its complex character or to decomposition; it is suggested that the gases obtained by Bedson from coals, probably arise from the decomposition of the resins in this manner. D. A. L.

Action of Cuprous Chloride on Potassium-iron Sulphide; Artificial Copper Pyrites. By R. SCHNEIDER (*J. pr. Chem.* [2], **38**, 569—582).—By shaking a faintly ammoniacal solution of cuprous chloride (equivalent to 0·455 gram of cuprous oxide) with potassium-iron sulphide, K_2S,Fe_2S_3 (1 gram), until the solution no longer contains copper, crystals are obtained which have the empirical formula $CuFeS_2$; but the quantity of the compound thus obtained and of the potassium chloride formed show that the formula of this sulphide is $Cu_2S.Fe_2S_3$, the equation for the reaction being $K_2S,Fe_2S_3 + Cu_2Cl_2 = 2KCl + Cu_2S,Fe_2S_3$.

These crystals behave almost identically with copper pyrites, and thus confirm the formula Cu_2S,Fe_2S_3 for copper pyrites, a view already adopted by the majority of chemists. A. G. B.

Artificial Production of Chromite. By S. MEUNIER (*Compt. rend.*, **107**, 1153—1154).—An intimate mixture of 148 grams of potassium dichromate, 58 grams of precipitated ferrous carbonate, and 56 grams of iron filings was heated to a very high temperature in a clay crucible for several hours. The following reaction takes place:— $FeCO_3 + 2Fe + K_2Cr_2O_7 = FeO,Cr_2O_3 + Fe_2O_3 + K_2CO_3$, and when the cooled product is treated first with water and then with concentrated acids, the chromite is left as a black, non-magnetic, granular residue. If the crucible is brasqued with a small quantity of cryolite, and the mixture is covered with a thin layer of the same mineral, the product shows distinct crystalline zones, one of which consists of specular hematite. The chromite is obtained in small octahedra, cubo-octahedra, and cubes. A small quantity of ferric chromate and of a double chromate of iron and potassium seems to be formed at the same time, and some lamellæ of chromic oxide are also observed. Similar results are obtained when powdered siderite is substituted for the precipitated ferrous carbonate. C. H. B.

Edisonite, a Fourth Form of Titanic Anhydride. By W. E. HIDDEN (*Amer. J. Sci.*, **36**, 272—274).—The original specimen of the mineral here described was discovered by the author in 1879 at the Whistnant gold mine, Polk Co., North Carolina. It was found in the concentrations of placer washings. The orthorhombic character of the mineral was easily proved with the hand-goniometer. The mineral has six cleavage planes, a hardness of 6, sp. gr. 4·26, resinous to adamantine lustre, bronze-yellow to golden-brown colour, and yellowish-white streak. It is insoluble in acids, unchanged before the blowpipe with sodium carbonate, but with borax gives a brownish bead. The axial ratio calculated by Des Cloizeaux is $\breve{a} : \bar{b} : c = 0·99275 : 1 : 0·92337$. On analysis, only titanic anhydride could be found. An analysis by S. L. Penfield has confirmed this conclusion. Owing to the scarcity of material, an equal weight of rutile was analysed by the same method as a check. The results were as follows:—

	Rutile.	Edisonite.
TiO_2 precipitated by boiling	0·0756	0·0744
Trace of oxide from the filtrate	0·0022	0·0033
Loss on ignition	0·0002	0·0001
Totals..................	0·0780	0·0778
Weight of mineral taken	0·0780	0·0770

These results show that edisonite is a nearly pure titanic anhydride like rutile. The author thinks he has recently identified this mineral on the Pilot Mountain, Burke Co., North Carolina, and proposes for it the name of edisonite, after T. A. Edison. B. H. B.

Artificial Production of Zircon. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **107**, 1000—1001).—Zircon was obtained by Deville and Claron by the action of zirconium fluoride on silica, or of silicon fluoride on zirconia, at a very high temperature. It can, however, be prepared at a temperature which need not exceed 700° by heating 11·88 grams of zirconia with 5·84 grams of silica and 100 grams of lithium bimolybdate. The same crystals are obtained at all temperatures between 700° and 1000°; they are hyaline, quadratic prisms with a brilliant lustre; sp. gr. = 4·6. If zirconia is in excess, the crystals are long: if silica is in excess, they are short.

Levy and Bourgeois used sodium carbonate at a very high temperature as a reagent for the detection of zirconium, zirconia being obtained in hexagonal prisms. With lithium molybdate and silica, easily recognisable crystals of zircon are obtained in a few hours at a temperature not necessarily exceeding 700°. C. H. B.

Beryllonite, a New Mineral. By E. S. DANA (*Amer. J. Sci.*, **36**, 290—291).—The author gives a preliminary notice of a new mineral, the locality of which is withheld for the present. The crystals belong to the orthorhombic system, the approximate axial ratio being $a : b : c = 0·57 : 1 : 0·94$. The mineral is white to colourless, transparent to translucent, and has a hardness of 5·5 to 6, sp. gr. 2·84, conchoidal fracture, and vitreous lustre. A preliminary analysis has shown the mineral to be an anhydrous phosphate of beryllium and sodium. B. H. B.

Xenotime. By W. E. HIDDEN (*Amer. J. Sci.*, **36**, 380—383).—The author describes crystals of xenotime found in the vicinity of 155th Street and 11th Avenue, New York City, in a coarse pegmatite vein; in some concentrations of vein material at Milholland's Mill, Alexander Co., North Carolina, and at Dysartsville, McDowell Co., North Carolina. He also describes xenotime-zircon from a new locality, namely, the Davis Land, Henderson Co., North Carolina. Of the 17 crystals of xenotime found at this locality, seven had zircons enclosed in parallel position. These symmetrically-compounded crystals of zircon and xenotime were first noticed by Zschau on specimens from Hitterö, Norway. Similar crystals have been found by the author at the Mills' gold mine, Burke Co., North Carolina, and at Deake tin mine, Mitchell Co., North Carolina. B. H. B.

Mineralogical Notes. By S. L. PENFIELD and E. S. SPERRY (*Amer. J. Sci.*, **36**, 317—331).—1. *Beryl.*—In order to prove the correctness of the assumption formerly made by the authors, that the alkalis, when present, replace the beryllium, analyses have been made of (I) the cæsium beryl from Norway, Maine; (II) a transparent yellow beryl, known as golden beryl, from Litchfield Co., Connecticut; and (III) a transparent, glassy variety from Willimantic, Connecticut, with very unusual crystalline habit. The results were as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	BeO.	Cs_2O.	K_2O.
I.	64·12	17·89	—	0·16	—	12·13	1·61	0·10
II.	65·62	17·86	0·37	0·18	—	13·50	0·03	—
III.	65·72	18·40	—	0·26	0·12	13·08	—	0·12

	Na_2O.	Li_2O.	Ignition.	Total.	Sp. gr.
I.	1·21	0·75	2·24	100·21	2·747
II.	0·54	0·10	2·34	100·54	2·716
III.	0·75	0·28	2·06	100·79	2·725

The results of analysis I afford the necessary proof of the correctness of the assumption that the alkalis in beryl are isomorphous with the BeO.

2. *Phenacite.*—Analysis of colourless phenacite from Topaz Butte, Pike's Peak region, Colorado, gave—

SiO_2.	BeO.	Na_2O.	Li_2O.	Ignition.	Total.
54·44	45·58	0·21	trace	0·26	100·49

3. *Monazite.*—Crystals of this mineral from a locality 3 miles east of the Emerald and Hiddenite mine, Alexander Co., North Carolina, gave, on analysis, the following results:—

P_2O_5.	Ce_2O_3.	$(LaDi)_2O_3$.	ThO_2.	SiO_2.	Ignition.	Total.	Sp. gr.
29·32	37·26	31·60	1·48	0·32	0·17	100·15	5·203

In opposition to the views of C. W. Blomstrand (this vol., p. 217), the authors do not regard the ThO_2 as an essential constituent of monazite, as it occurs in varying proportions, although almost always present in the different varieties.

4. *Sussexite.*—A new analysis of this rare mineral from Maine Hill, Franklin, New Jersey, fully substantiates the formula $H(Mn,Mg,Zn)BO_3$, determined by G. J. Brush, who first described the mineral.

The authors also describe (5) twin crystals of quartz with inclined axes, said to be from Madagascar, and give long descriptions and analyses of (6) oligoclase from Bakersville, North Carolina, with abnormal optical properties; (7) barium felspar from Blue Hill, Delaware Co., Pennsylvania; and (8) a very pure magnesia mica, phlogopite, from Edwards, St. Lawrence Co., New York.

B. H. B.

Ferric Orthoclase. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **107**, 1150—1152).—A mixture of 78 parts of normal potassium vanadate and 10 parts of potassium nitrate is fused at 700°, and a mixture of 18 parts of silica and 8 parts of ferric oxide is gradually added and well mixed by means of a platinum wire. Mineralisation is very soon complete, and the first product is a ferric leucite, but if the mixture is kept at 700° for about a month, crystals separate in the fused mass. After cooling, the product is extracted with water and the residue is treated with cold concentrated potash. Ferric orthoclase, $K_2O,Fe_2O_3,6SiO_2$, is thus obtained in monoclinic prisms, frequently macled in the same way as orthoclase, and with the same optical properties. They show the faces p, m, g', a', $a^{\frac{1}{2}}$, $o^{\frac{1}{2}}$, $b^{\frac{1}{2}}$, the angles m/m 118° 58′ and p/m 112° 44′, being practically identical with those of orthoclase. Some ferric microcline seems to be formed at the same time.

C. H. B.

Geology of the District of Ričan. By F. KATZER (*Chem. Centr.*, 1888, 1493, from *Jahrb. geol. Reichsanst. Wien.*, **38**, 355—415).—The district of Ričan, south-east of Prague, consists of granite and clay-slate of the Cambrian formation. The granite, principally porphyritic, contains partly white, partly red orthoclase crystals (containing calcium) 8—10 cm. long, with biotite, and a little plagioclase and accessory apatite, tourmaline and titanite. As the clay formation nears the granite, it becomes harder and more crystalline, whilst, on the other hand, the granite near the juncture with the clay becomes more porphyritic. Close to the granite is a massive layer of chert. This is rich in quartz with liquid inclusions. The following analyses are given by the author:—

	Normal clay-slate.	Blackened slate.	Chert.
SiO_2	54·97	61·35	84·19
H_2O	4·22	3·07	1·70

The author subdivides the strata as follows:—(*a.*) Contact zone, containing little mica and no tourmaline; (*b*) granitic pegmatite, rich in tourmaline; (*c*) porphyritic granite, containing biotite, felspar, and granitic tourmaline. The latter is 100 m. thick in places; the pegmatite is regular, and measures 6 metres throughout. The following further analyses were made:—(1.) Biotitic granite, 8 cm. from the juncture; (2) tourmalinic pegmatite, 3 metres from the contact; (3) normal granite of Zeruovka.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	B_2O_3.	H_2O.
I.	74·29	15·95		trace	0·78	0·66	5·31	2·66	—	0·66
II.	75·27	12·92	1·89	0·29	0·32	0·47	6·48	1·14	1·24	0·61
III.	71·13	18·53		trace	0·96	0·58	7·26		—	0·74

J. W. L.

Two New Masses of Meteoric Iron. By G. F. KUNZ (*Amer. J. Sci.*, **36**, 275–277).—1. A mass of meteoric iron was found in 1882 on Linville Mountain, Burke Co., North Carolina. The meteorite weighs 428 grams, the original weight having been 442 grams. It is 2⅗ inches long, 1⅗ inch high, and 2½ inches wide. One side is rather rough, and the other covered with very shallow pittings. Traces of the black crust of magnetic oxide are still visible. The iron admits of a very high polish, and, under the glass and by reflected light, appears to be a network of two distinct bodies. On analysis, it gave the following results:—

Fe.	Ni.	Co.	S.	C.	P.	Total.
84·56	14·95	0·33	0·12	trace	trace	99·96

It most closely resembles the Tazewell (Claiborne Co.) and Bear Creek meteorites in composition.

2. In 1887, a mass of meteoric iron was found in the Silver Crown district, Laramie Co., Wyoming. When found, it was half buried in decomposed granite and earth. In shape, it somewhat resembles an anvil. It weighs 25·61 lbs. The surface is still covered with the original crust of magnetic oxide, and is irregularly pitted. This iron belongs to the braunite group of Meunier. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	C.	Total.	Sp. gr.
91·57	8·31	trace	0·07	trace	99·95	7·63

In composition it most closely resembles the Rowton, Charlotte, and Jewel Hill meteorites. B. H. B.

Meteorite from Ochansk. By TICHONRAVOFF, PETROFF, and others (*J. Russ. Chem. Soc.*, 1888, **20**, 513—518).—This meteorite, together with other smaller ones, fell on April 18 (old style), 1887, near Tabory, Ochansk, in the Government of Perm. Its original weight was about 120 lbs., and it was found in a very hot state about 2 yards in the ground. The meteorite was covered with a black, glistening crust, and its mass was ash-grey; structure crystalline. It dissolves in hydrochloric acid with evolution of hydrogen and hydrogen sulphide, owing to the presence of free nickel-iron and troïlite (magnetic pyrites). The glistening black grains were found to be meteoric iron, containing Fe = 79·10—74·19, Ni 20·9—25·81 per cent.

It contains only 0·05 per cent. phosphorus, probably in the form of schriebersite (Fe_4Ni_2P). Its percentage in the meteorite varies from 20·54 to 25·02 per cent., owing to the non-homogeneity of the mass of the meteorite. The mean composition of the meteorite, according to four analyses, is—

SiO_2.	FeO.	MgO.	CaO.	Fe.	Ni.	S.
37·36	13·80	18·54	3·00	19·80	5·55	2·30

P.	C amorphous.	Cu + Sn.	Mn, Co, Na.
0·05	0·08	0·52	traces

Assuming that all the sulphur is present as Fe_7S_8, the amount would be 8·17 per cent., and that of the FeO only 7·41 per cent.

B. B.

The Chemical Composition of the Water composing the Clyde Sea Area. By A. DICKIE (*Proc. Roy. Soc. Edin.*, **127**, 283—286).

Organic Chemistry.

Action of Mercuric Cyanide on Cupric Salts. By R. VARET (*Compt. rend.*, **107**, 1001—1002).—When an aqueous solution of mercuric cyanide is boiled with an equivalent quantity of any oxy-salt of copper, no cyanogen is evolved, and no cuprous cyanide is precipitated. Double salts are formed, and crystallise on cooling.

If a concentrated solution of mercuric cyanide is mixed with half the equivalent quantity of cupric chloride below 25°, and the saturated solution is cooled in a freezing mixture, it very slowly deposits small, transparent, blue needles, of the composition

$$2HgCy_2,CuCl_2 + 6H_2O.$$

They are very deliquescent, and dissolve readily in water and ammonia solution. Above 30° the mixture of mercuric cyanide and cupric chloride evolves cyanogen, and, if the solution is dilute, cuprous cyanide is precipitated, but if it is concentrated, a double cyanide of copper and mercury is obtained.

A concentrated solution of mercuric cyanide and cupric chloride in equivalent proportions deposits hard, green, efflorescent crystals of the compound $HgCy_2,CuCl_2 + 6H_2O$, less soluble in water than the preceding compound, but readily soluble in ammonia. At 35°, the solution evolves cyanogen, and yields a precipitate of the composition $Cu_2Cy_2,CuCy_2 + H_2O$, which at a higher temperature is converted into cuprous cyanide.

Hot solutions of haloïd cupric salts are decomposed by mercuric cyanide, with evolution of cyanogen, and formation of compounds of mercuric salts and cuprous cyanide which will be described subsequently. The same compounds are obtained without evolution of cyanogen, by the direct action of mercuric salts on cuprous cyanide.

C. H. B.

A New Potassium Iron Cyanogen Compound. By F. MAHLA (*Ber.*, **22**, 111—114).—When a cold, aqueous extract of the substance (?) used in the purification of gas is fractionally precipitated with ferric chloride, a dark-violet substance is at last obtained, which differs from Prussian blue in many of its properties. It is decomposed by alkalis with separation of ferric hydroxide, and on adding acid to the yellow solution, the substance again separates as a splendid violet precipitate, and when the solution is not too dilute, the whole solidifies to a gelatinous mass. The *potassium salt*, which is prepared by treating the well-washed violet precipitate with potash free from chloride, keeping the solution neutral, crystallises in indistinct, bright-yellow, tabular crystals, resembling potassium ferrocyanide; it is almost insoluble in ether, very sparingly soluble in alcohol. The crystals contain water of crystallisation, the whole of which cannot be removed without decomposition of the salt. Dilute sulphuric acid decomposes it with evolution of hydrogen cyanide; when heated with strong sulphuric acid, it is converted into ammonium sulphate and carbon monoxide. The aqueous solution yields with ferric chloride a violet, with copper salts a parrot-green, and with silver salts, stannous chloride, lead acetate and mercuric chloride white precipitates. Analyses of the potassium salt pointed to the formula $K_2\!:\!C_3N_3\cdot Fe\cdot C_2N_2\cdot K$.

In determining the carbon in the potassium salt, the substance was mixed with alumina, which combines with potash, so that the whole of the carbonic anhydride passes off. N. H. M.

New Method of Obtaining Cyanethine and Similar Bases. By E. v. MEYER (*J. pr. Chem.* [2], **38**, 584).—Ethyl cyanide is heated with dry sodium ethoxide in a tube at 140°, and the product treated with water; the ethyl cyanide is thereby mostly converted into cyanethine. The subject is under investigation. A. G. B.

Action of Alcoholic Potash on Allylene. By A. FAVORSKY (*J. Russ. Chem. Soc.*, 1888, **20**, 518—523).—In previous papers (Abstr., 1888, 798 and 1168), the author has shown that monosubstituted acetylenes when acted on by alcoholic solution of the alkalis are converted into disubstituted acetylenes or non-symmetrical allenes. It was, however, impossible to prove the existence of intermediate mixed tertiary ethers of the general formula $CHR\!:\!C(OEt)\cdot CH_3$ or $R_2CH\cdot C(OEt)\!:\!CH_2$. In this respect it was interesting to investigate allylene as the simplest of the monosubstituted acetylenes. Allylene was prepared by the action of alcoholic potash on propylene bromide, using a reflux condenser, and the gas absorbed in ice-cold absolute alcohol. The saturated solution was then heated in sealed tubes with solid potash for 12 hours at 170—180°. On opening the tubes, much of the allylene was found to be unchanged, and on addition of water, an oily layer separated, which was found to distil between 62° and 63°. Its sp. gr. is 0·790 at 0° and 0·769 at 20°. It consisted of ethyl isopropenyl ether, $CH_3\cdot C(OEt)\!:\!CH_2$. The same compound is obtained directly by the action of alcoholic potash on propylene bromide at 170—180°. When treated with concentrated hydriodic acid, it is completely resinified. With sulphuric acid of 2, or better, of 1 per cent., the ether even at the ordinary temperature yields acetone and ethyl alcohol. By this behaviour it is distinguished from ethyl allyl ether (b. p. 62·5°), which with hydriodic acid yields ethyl and allyl iodides (Oppenheim), and with sulphuric acid of 2 per cent. ethyl and allyl alcohols (Eltekoff). The ether is formed by the direct addition of allylene and alcohol, and represents an intermediate product, as was expected by the author. The intermediate product was not isolated in other cases quoted above, as the temperature (130—140°) was sufficient for the decomposition of the analogous compounds produced. Further investigations will show whether the tertiary ethyl isopropyl ether is stable, and whether, like its homologues, it decomposes into alcohol and allene. B. B.

Butines. By L. M. NORTON and A. A. NOYES (*Amer. Chem. J.*, **10**, 430—433).—The fourth possible butine, *methylisoallylene*, $CH_3\cdot CH\dot{:}C\dot{:}CH_2$, is prepared from butyric chloral, itself prepared from croton chloral hydrate. The butyric chloral, $CH_3\cdot CHCl\cdot CCl_2\cdot CHO$, was treated in the cold with zinc ethyl, and the product when decomposed by dilute acid gave trichlorobutyl alcohol, which by heating with phosphorus pentachloride yields methylisoallylene tetrachloride, $CH_3\cdot CHCl\cdot CCl_2\cdot CH_2Cl$, and also $\alpha\alpha\beta$-trichlorbutyl phosphate, a substance crystallising from alcohol and melting at 85·3°. The former substance, when treated in alcoholic solution with the copper-zinc couple, yields methylisoallylene, a colourless liquid boiling at 18—19°; it does not precipitate an ammoniacal cuprous solution, and with bromine yields first a dibromide and then a tetrabromide, both being liquids. H. B.

Heptine from Perseitol. By MAQUENNE (*Compt. rend.*, **108**, 101—103).—The heptine obtained from perseitol by the action of hydriodic acid (this vol., p. 32) is attacked by sulphuric acid even at 0°, when it becomes brown, and is partially converted into a polymeride, $C_{14}H_{24}$, and partially into a resin which gives a green solution with alcohol. Concentrated hydriodic acid at the ordinary temperature yields a crystallisable hydriodide, $C_7H_{13}I$, which can be distilled in a vacuum, and yields the original hydrocarbon on treatment with potash; at 150° it is converted into complex polymerides. Chlorine acts destructively on the hydrocarbon, and bromine acts violently in the cold with formation of a dibromide, $C_7H_{12}Br_2$, which soon decomposes and becomes green. Mercuric chloride is slowly attacked with formation of a rose-grey precipitate changing to black, but ammoniacal silver and cuprous solutions are not affected. Nitric acid acts violently, and produces resinous products and acetic and butyric acids. When exposed to air, the hydrocarbon oxidises, and in 10 days will absorb 100 times its volume of oxygen. If the product is distilled, it yields a hydrate, $C_7H_{14}O_2$, which crystallises from water in long, white, seemingly quadratic needles. The same product is obtained by allowing the hydrocarbon to remain in contact with a small quantity of water in a loosely corked flask.

The heptine obtained from perseitol is identical with that obtained by Renard (*Ann. Chem. Phys.* [6], 1, 223) and by Morris from resin (Trans., 1882, 174). With concentrated hydrochloric acid at 150°, both products yield a crystalline hydrochloride, $C_7H_{13}Cl$, which boils at 55° in a vacuum, and yields the original heptine when treated with potash, alcoholic ammonia, acetates, or zinc ethyl. It is at once coloured by bromine, but can only be attacked by substitution.

The properties of this heptine indicate that it has a closed chain nucleus, and is not methylpropylallylene, as supposed by Morris.

The tendency to oxidise, form a hydrate, and polymerise indicates that it is related to the terpenes, whilst the formation of green compounds on oxidation points to a relationship with furfuran. It would seem, therefore, that heptine from perseitol is a non-saturated hydrocarbon with a tetramethylene nucleus. The relation between this heptine and the terpenes, and the fact that it is obtained both from resin and from perseitol, seems to point to a connection between the sugars and the resins. C. H. B.

Diisocrotyl and several of its Derivatives. By S. PŘIBYTEK (*J. Russ. Chem. Soc.*, 1888, **20**, 506—512).—*Diisocrotyl*, a hydrocarbon, C_8H_{14}, of the diallyl series, is obtained by the action of sodium on isocrotyl bromide, $CMe_2{:}CHBr$, in the following manner. Isobutylene is converted into its dibromide, and this, on treatment with alcoholic potash, yields isocrotyl bromide (b. p. 91—96°); the latter is poured on to metallic sodium covered with a layer of ether and contained in tubes, but as a violent reaction takes place after the lapse of 15—20 minutes, the tubes have to be carefully cooled before sealing up. The sealed tubes are then placed for five days in water of the ordinary temperature, and are afterwards exposed to the temperature of 30—40° for 10 days, until no further diminution of volume (amounting to one-fifth of the whole liquid) is found to take place. On opening the tubes, a gas, consisting chiefly of isobutylene, escapes under great pressure. After separating the sodium and sodium bromide by filtration, and the ether by distillation, the liquid product of the reaction boils between 120° and 150°, leaving a resinous mass containing sodium. It is difficult to obtain a product of constant boiling point, as the hydrocarbon shows an inclination to polymerisation; so that on repeating the distillation several times, the boiling point becomes lower, and after a lapse of some time it again becomes higher. The same is the case as regards the melting point. The freshly distilled hydrocarbon boils at 125—130°, solidifies at 0°, and the crystals melt at 4° to 5°, but after several months the melting point becomes 12° to 22°. The hydrocarbon absorbs oxygen very eagerly; 1 c.c. was found to absorb 17·7 c.c. of oxygen over mercury. The molecular formula is C_8H_{14}, sp. gr. = 0·7726 at 18°. By treating it with bromine, a liquid tetrabromide, $C_8H_{18}Br_4$, was obtained. From this, as well as from the formation of an oxychlorhydrin by the addition of hypochlorous acid and oxygen, the structure $CMe_2{:}CH{\cdot}CH{:}CMe_2$ is derived.

The chlorhydrin, $C_8H_{14}OCl{\cdot}OH$, is a colourless liquid, soluble in ether; the solution in ether, on treatment with dry potassium hydroxide, yields the impure dioxide, $C_8H_{14}O_2$, and this with water forms a crystalline tetrahydroxide, $C_8H_{14}(OH)_4$—the erythrol of the octyl series. The same erythrol was obtained on heating the diisocrotyl chlorhydrin with water and lead oxide at 100° in sealed tubes. Its melting point is 152—154°. B. B

Action of Iodine, Iodoform, and Methylene Iodide on Sodium Ethoxide and that of Iodine on Ethyl Sodium Carbamate. By E. Mulder (*Rec. Trav. Chim.*, **7**, 310—333).—The action of iodine on sodium ethoxide was studied by Butlerow, who found, as chief products, iodoform and methylene iodide. The author has further investigated the nature of the reaction, and finds that it may be represented by the following stages:—(A) $C_2H_5{\cdot}ONa + I_2 = C_2H_5{\cdot}OI + NaI$; (B) $C_2H_5{\cdot}OI = CH_3{\cdot}COH + HI$; (C) $C_2H_5{\cdot}ONa + HI = C_2H_5{\cdot}OH + NaI$; (D) $CH_3{\cdot}COH + 3C_2H_5{\cdot}OI = CI_3{\cdot}COH + 3C_2H_5{\cdot}OH$. The iodal is then decomposed by the sodium ethoxide with formation of iodoform and ethyl formate. By the action of iodoform on sodium ethoxide, methylene iodide and other secondary products are produced. Methylene iodide has no appreciable action on sodium ethoxide at the ordinary temperature.

The products of the reaction of iodine with ethyl sodium carbamate are found to be iodoform and urethane. The iodoform has no further action in alcoholic solution, and secondary products are therefore not produced.

It is found that iodoform is dissolved by hydriodic acid in appreciable quantity in alcoholic, but not in aqueous solution. The maximum amount of iodoform is obtained from sodium ethoxide with $1\frac{3}{10}$ mol. I to 1 mol. of the ethoxide. H. C.

Action of Methyl Iodide on Sodium Arsenite. By H. Klinger and A. Kreutz (*Annalen*, **249**, 147—155).—The authors confirm the accuracy of G. Meyer's statement (Abstr., 1883, 1078) that the products of the action of methyl iodide on sodium arsenite are sodium iodide and sodium methyl arsenate. *Methylarsendisulphide*, $AsMeS_2$, is obtained by passing hydrogen sulphide through the hot acid solution of the sodium salt. It is a thick, gum-like mass having a disagreeable smell, and is decomposed by heat into methyl sulphide and arsenic sulphide. Nitric acid oxidises it to methylarsenic acid, and sulphur is liberated. W. C. W.

Ethyl Fluoride. By H. Moissan (*Compt. rend.*, **107**, 992—994).—When dry ethyl fluoride is heated to dull redness in a glass bulb for several hours, it yields a complex mixture of hydrocarbons containing only traces of silicon fluoride. A feeble induction spark causes considerable expansion, and the products are hydrogen fluoride, ethylene, and a small quantity of acetylene, but no free carbon. Strong induction sparks produce a deposit of free carbon and a gaseous mixture of acetylene, ethylene, propylene, &c. If the ethyl fluoride is passed slowly through a platinum tube heated to dull redness, it yields hydrogen fluoride, and hydrocarbons which are partly soluble in concentrated sulphuric acid, whilst those not absorbed by the acid are partly absorbed by bromine-water. Inside the tube there is a deposit of a small quantity of carbon, readily soluble in nitric acid and potassium chlorate.

Inhalation of ethyl fluoride by a guinea-pig, produces at first a period of excitement, but this is soon followed by death.

The fluoride was analysed by burning it in a metal tube by means of a mixture of cupric oxide and lead oxide. Dry ethyl fluoride does not attack glass, but it dissolves in concentrated sulphuric acid, and this solution acts on the glass with formation of an equivalent quantity of silicon fluoride. The latter is insoluble in sulphuric acid, and measurement of its volume determines the quantity of fluorine in the original compound. The results agree with the formula C_2H_5F.

C. H. B.

Methyl and Isobutyl Fluorides. By H. MOISSAN and M. MESLANS (*Compt. rend.*, **107**, 1155—1157).—Dumas and Peligot obtained methyl fluoride by the action of methyl hydrogen sulphate on potassium fluoride, but the authors find that the product of this reaction is a mixture of methyl fluoride and methyl oxide, which can be separated by their difference in solubility. Better results are obtained by the action of methyl iodide on silver fluoride, the gas being passed through a lead tube cooled at —50°, and over silver fluoride heated at 90°. Methyl fluoride is not formed by the action of phosphorus pentafluoride or hydrofluoric acid on methyl hydroxide. The properties of the compound agree with the description given by Dumas and Peligot. Its sp. gr. is 1·22 (calc. 1·19), it liquefies under 30 atmos. at the ordinary temperature, and is only slightly soluble in water, but more soluble in methyl alcohol and methyl iodide. It is very stable, and is only very slowly saponified by water or dilute potash in sealed tubes at 120°. (Compare Collie, Trans., 1889, 110.)

Isobutyl fluoride is obtained in a similar manner; it is a liquid which boils at 16° under atmospheric pressure. The gas burns with a very smoky flame with formation of hydrogen fluoride. When dry, it does not attack glass; it is very soluble in alcohols and ethers; sp. gr. at 21° = 2·58 (calc. 2·66). Below 16°, it condenses to a colourless, very mobile liquid, which has not a pleasant odour, does not attack glass if quite dry, and dissolves small quantities of sulphur and phosphorus, and considerable quantities of iodine and bromine.

All these fluorine-derivatives are more stable than the corresponding chlorine-derivatives, and boil at a lower temperature.

C. H. B.

Isobutyl Nitrite. By W. R. DUNSTAN and E. J. WOOLEY (*Pharm. J. Trans.* [3], **19**, 487).—Isobutyl nitrite was prepared by gradually mixing isobutyl alcohol with sulphuric acid; when cold, the mixture was poured, in small quantities at a time, to the bottom of an aqueous solution of sodium nitrite (1 : 3), the whole being kept cool. Isobutyl nitrite immediately separated as an ethereal layer, and was decanted, washed with solution of potassium carbonate, and digested with fused potassium carbonate. It is a pale-yellow, slightly fragrant liquid, sp. gr. 0·876 at 15° (water at 15° = 1), and boils at 67°. It is apt to become acid when kept, especially in presence of moisture, and when acid is once formed, decomposition ensues rapidly. This, however, is greatly retarded by keeping a fragment of sodium hydrogen carbonate in the liquid. Administered to animals, isobutyl nitrite brings about a rapid fall of blood-pressure, an acceleration of the pulse, and a powerful respiratory paralysis.

R. R.

The Metameric Amyl Nitrites. By W. R. DUNSTAN and W. L. WILLIAMS (*Pharm. J. Trans.* [3], **19**, 487—489).—The liquid hitherto known as amyl nitrite is a mixture of metameric nitrites corresponding respectively with the isobutyl carbinol (α-amyl alcohol) and the secondary butyl carbinol (β-amyl alcohol) contained in various proportions in the "amyl alcohol" from which it has been prepared. The authors describe the process by which they obtained from the 127—132° fraction of fusel oil, a mixture of these two amyl alcohols free from other substances. This mixture had a lævorotatory power that indicated the presence of 15·4 per cent. of secondary butyl carbinol, the other alcohol being optically inactive. A mixture of the two nitrites obtained from this was, however, dextrorotatory from the action of the β-amyl nitrite, and its physiological effect was like that of isobutyl nitrite, but less powerful. These nitrites could be obtained separately only by previous isolation of the corresponding alcohols, and this was effected by converting the mixture into barium amyl sulphates and taking advantage of the smaller solubility of the α-amyl salt. It was only after 35 recrystallisations, that, on regenerating the alcohol from the barium salt, practically pure isobutyl carbinol was obtained. The nitrite prepared from this was an optically inactive, pale-yellow liquid of sp. gr. 0·880, b. p. 97°. It had a not disagreeable odour, and when inhaled, produced the characteristic nitrite effect. Its exact physiological action is under further investigation. R. R.

Action of Alkalis on the Nitro-compounds of Alkyl Radicles. By N. SOKOLOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 498—500).—In reference to the interesting reaction which takes place between nitroethane and soda or ammonia, the author has investigated its homologues from the same point of view. Nitromethane was heated with ammonia in sealed tubes at 100°, when the mixture became brown. Nitrous acid was found to be present in the liquid, but no other definite products of the reaction could be isolated. As the reaction between nitropropane and alkalis is far more feeble, it was heated with alcoholic potash for 4—5 hours at 140°. The product is a liquid, $C_9H_{15}NO$, of sp. gr. 0·961, boiling at 217—220°. Nitro-isopropane enters more easily into reaction with ammonia or soda, and the product consists chiefly of pseudopropylnitrol, together with much nitrite, but no compound analogous to $C_9H_{15}NO$ is formed.

B. B.

Action of Alkyl Iodides on Sodium Nitroethane. By N. SOKOLOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 579—582).—In former papers (*J. Russ. Chem. Soc.*, 1886, 274, and 1887, 384), the author has shown that the following reactions take place between nitroethane and alkaline hydroxides or carbonates in alcoholic or aqueous solutions: (1) $3C_2H_5NO_2 + NaOH + 2C_2H_6O = C_6H_9NO + NaNO_2 + 2C_2H_4O + NH_3 + 4H_2O$, and (2) $6C_2H_5NO_2 + 3NaOH = 2C_6H_9NO + 3NaNO_2 + NH_3O + 6H_2O$. The equations were confirmed by the quantitative determination of the products of reaction. As the compound C_6H_9NO and its homologues C_4H_5NO, C_5H_7NO, and $C_7H_{11}NO$ were obtained by Götting (Abstr., 1888, 355) by the action of alkyl iodides on sodium nitroethane in alcoholic solution, the author has repeated these experiments, employing V. Meyer's and Wurster's methods. The iodides of methyl, ethyl, propyl, and isobutyl were heated with dry sodium nitroethane in closed vessels in a water-bath, but it was found that no action took place. After treatment with water and boiling the aqueous solution, the compound C_6H_9NO could be extracted with chloroform. With other alkyl iodides, it was also found that there was no change. The same experiments were repeated in the presence of alcohol of 90—99 per cent., and then a reaction took place. The same was observed when sodium ethoxide was heated with nitroethane and the alkyl iodide. After dilution with water, the compound C_6H_9NO was extracted with chloroform and purified by distillation with steam. It is a yellow, oily liquid, boiling at 171°, whereas the pure substance obtained from sodium nitroethane and alcohol or water boils at 175°. Sp. gr. = 1·00023 at 0°. From methyl iodide or ethyl iodide, one and the same compound, C_6H_9NO, was obtained. The author concludes that: (1) alkyl iodides gives no reaction with sodium nitroethane; (2) the reaction described by Götting is due to the presence of ethyl alcohol, the alkyl iodides have only a disturbing action; (3) the compound C_6H_9NO obstinately retains water and alcohol, with which it parts near its own boiling point only; to this cause may be due the fact that Götting, on analysing such mixtures, obtained results agreeing with the formulæ C_4H_5NO, C_5H_7NO, and $C_7H_{11}NO$. The author claims priority in the discovery of the compound C_6H_9NO (see Abstr., 1888, 797). B. B.

Nitroethyl Alcohol. By R. Demuth and V. Meyer (*Ber.*, **21**, 3529—3530).—*Nitroethyl alcohol*, $NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is prepared by the action of silver nitrite on ethylene iodohydrin, and is purified by means of the sodium salt; this is dissolved in water, treated with sulphuric acid, and extracted with ether. The compound behaves like an alcohol, and is miscible with water. It yields azo-dyes; the compounds $N_2Ph{\cdot}CH(NO_2){\cdot}CH_2{\cdot}OH$ and $SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}CH(NO_2){\cdot}CH_2{\cdot}OH$ were prepared and analysed. The *sodium salt*, $NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}ONa$, is an explosive substance insoluble in water. N. H. M.

Butyric Ethers. By E. Reboul (*Compt. rend.*, **108**, 39—43).—The four butyl alcohols were converted into sodium-derivatives in the usual way, care being taken to avoid access of air. With the tertiary alcohol, the reaction takes place slowly, and the liquid must be heated for some time. All four compounds separate in crystals containing 2 mols. of the particular alcohol, which is expelled by heating at 200—220°, or by placing the crystals in a vacuum over sulphuric acid, or by subjecting them to a current of purified and dry hydrogen or air. The dried sodium-alkyl oxides are decomposed by water into the corresponding alcohol and sodium hydroxide, but even when the compounds have been heated to 220° they have experienced no isomeric change, and the alcohol which they yield on treatment with water is identical with that from which they were formed. At 210—220°, the tertiary compound sublimes in bulky, slender, white needles, and the secondary compound shows signs of sublimation.

The ethers were prepared by the action of butyl bromides on a slight excess of the sodium-derivatives. In addition to the ether and sodium bromide, a butyl alcohol and butylene are formed, and this secondary reaction, which is comparatively slight in six cases, becomes the predominant if not the only reaction in the other four cases. The following ethers were obtained in this way :—

	B. p.	Sp. gr.
$O(CH_2{\cdot}CH_2{\cdot}CH_2Me)_2$	141°	0·784 at 0·0°
$CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}O\ CH_2{\cdot}CHMe_2$ ..	131·5—132°	0·763 at 15·5
$CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CHMe{\cdot}CH_2Me$	131·0—131·5	0·7687 at 15·0
$CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CMe_3$	124·0—125·0	

With hydrobromic acid, all the ethers yield water and the bromobutanes corresponding with the alcohols from which they were formed. The boiling point of the last ether in the list differs from that of the normal ether by only 16—17°, whilst the difference in the case of the alcohols is 33°, and in the case of the bromobutanes 30°.

C. H. B.

Compound of Monosodium Glycol with Glycol. By De Forcrand (*Compt. rend.*, **107**, 1160—1162).—23 grams of sodium is added very gradually to 124 grams of glycol, and when the reaction is nearly complete the liquid is heated at 150° until all the sodium dissolves. When the liquid cools, it forms a mass of dry, colourless, very brilliant crystals of the composition $C_2H_5NaO_2,C_2H_6O_2$. Heat of dissolution in water at 20° = +0·70, and from the thermal data obtained by the action of sodium on glycol—

$2C_2H_6O_2$ liq. + $\frac{1}{2}Na_2O$ sol. = $\frac{1}{2}H_2O$ sol. + $C_2H_5NaO_2,C_2H_6O_2$ sol. .... develops +31·245 Cal.

$C_2H_5NaO_2$ solid + $C_2H_6O_2$ liquid = $C_2H_5NaO_2,C_2H_6O_2$ sol................ „ +7·025 „

The heat of formation of this compound from its proximate constituents is higher than that of any alcoholate except the methyl alcoholate of sodium methoxide.

C. H. B.

Molecular Weight of Arabinose and Xylose. By B. Tollens, F. Mayer, and H. Wheeler (*Ber.*, **21**, 3508—3510).—The following results were obtained by Raoult's method: for dextrose, 188·7; for arabinose, 155·1; for xylose (wood-sugar), 154·1. In determining the molecular weight, very uniform results are obtained if the vessel when taken out of the freezing mixture is dried and surrounded with cotton-wool.

N. H. M.

Platinum Compounds of Propyl and Isopropyl Sulphides. By C. Rudelius (*J. pr. Chem.* [2], **38**, 497—512; compare this vol., p. 230).—*Platosopropylsulphine α-chloride*, $PtCl{\cdot}SPr_2{\cdot}SPr_2Cl$, is obtained by the action of propyl sulphide on a solution of potassium platinosochloride; it is soluble in chloroform, ether, and absolute alcohol (6·5 parts at 15°), and crystallises in large, yellowish-red crystals melting at 46°. The *β-chloride*, $Pt(SPr_2Cl)_2$, crystallises in pale yellow, monosymmetrical prisms soluble in alcohol, and melting at 86°. The γ-*chloride* forms pale-yellow, thin, rhombic laminæ, soluble in the usual solvents and melting at 63°.

Platosethylpropylsulphine iodide, $SEt_2I \cdot Pt \cdot SPr_2I$, forms red, rhombic prisms [$a : b : c = 1 \cdot 7270 : 1 : 4 \cdot 1729$], melting at 115°. *Platosopropylisopropylsulphine iodide* forms long, slender, rhombic crystals melting at 131°. *Platosethylisopropylsulphine iodide* crystallises in short, thick crystals.

Platosopropylsulphine α-hydroxychloride, $PtCl \cdot SPr_2 \cdot SPr_2 \cdot OH$, is obtained by the action of alcoholic potash (1 mol.) on the α-chloride; it forms a semi-solid mass which gradually crystallises. The *α-iodochloride* forms long, prismatic crystals, soluble in chloroform and alcohol. The *bromide*, $Pt(SPr_2Br)_2$, forms long, yellowish-brown, rhombic prisms, soluble in ether, chloroform, and alcohol, and melting at 105°; the *iodide* forms long, red, rhombic prisms melting at 133°. The *α-* and *β-nitrites*, the *α-nitrate*, *basic α-nitrate*, *β-nitrate*, *β-sulphate*, *β-chromate*, *β-oxalate*, and *β-thiocyanate* are also described.

Of double salts, the author describes *platosopropylsulphine platinosochloride*, the *platinoso-iodide* and *mercurochloride*.

Platinipropylsulphine chloride, $PtCl_2(SPr_2Cl)_2$, is obtained from the platoso-α-chloride and chlorine; it crystallises in long, bright yellow, monoclinic prisms, soluble in alcohol and chloroform, and melting at 139°. The *bromide* forms long, dark red, monoclinic prisms melting at 141°. The *bromochloride* forms yellowish-red, prismatic crystals melting at 129°; the *iodide* and *hydroxy-nitrate* are also described.

Platosoisopropylsulphine chloride, $Pt(SPr^{\beta}_2Cl)_2$, forms long, yellow, triclinic crystals melting at 163°, and soluble in chloroform, ether, and alcohol. The *bromide*, *iodide*, *thiocyanate*, and *nitrite* are described.

Platinisopropylsulphine iodide, $PtI_2(SPr^{\beta}_2I)_2$, forms dichroic crystals, soluble in chloroform and alcohol and melting at 139°.

A. G. B.

Platinum Compounds of Butyl, Isobutyl, and Benzyl Sulphides. By H. LÖNDAHL (*J. pr. Chem.* [2], **38**, 512—523).—*Platosobutylsulphine α-chloride*, $PtCl \cdot SBu_2 \cdot SBu_2Cl$, forms large, orange-yellow, asymmetrical crystals, soluble in alcohol and ether and melting at 40°. The *β-chloride*, $Pt(SBu_2Cl)_2$, forms greenish-yellow, four-sided, asymmetrical tables melting at 77°. The γ-*chloride* is semi-solid at the ordinary temperature, and melts at 17—20°. The *bromide*, $Pt(SBu_2Br)_2$, crystallises in brownish-yellow, rhombic tables melting at 65°, and the *iodide* in dark red, rhombic tables melting at 65°. The *nitrite* and *nitrate* are described.

Platinibutylsulphine chloride, $PtCl_2(SBu_2Cl)_2$, is obtained by the action of chlorine on the platoso-α-chloride, and forms small, yellow crystals.

Platosoisobutylsulphine α-chloride crystallises in thin, four-sided, rhombic tables melting at 83°. The *β-chloride* forms oblique, four-sided, greenish-yellow, monoclinic tables, soluble in alcohol and ether and melting at 139°. The *bromide* crystallises in thin, hexagonal tables melting at 143—144°, and the *iodide* in hexagonal, rhombic tables melting at 187°. The *α-nitrite*, *β-nitrite*, *α-chloronitrate*, *β-nitrate*, *β-sulphate*, and *β-chromate* are also described. The *hydroxide*, $Pt(SBu^{\beta}_2 \cdot OH)_2$, is obtained as a viscous substance by the action of barium hydroxide on a sulphuric acid solution of the β-sulphate; its solution is alkaline.

Platinisobutylsulphine chloride, $PtCl_2(SBu^{\beta}_2Cl)_2$, crystallises in thick, yellow, hexagonal tables melting at 162°. The *bromide* forms red, monoclinic prisms or tables melting at 184°. The *bromochloride* and *chlorobromide* are described. A *periodide*, $PtI_2(SBu^{\beta}_2I)_2,I_2$, is obtained by the action of iodine on a chloroform solution of the β-iodide; it forms large, dark prisms and is converted into the β-iodide at 110°. A similar *periodochloride* is described. *Diplatinisobutylsulphine iodochloride*, $PtI(SBu^{\beta}_2Cl)_2,PtI(SBu^{\beta}_2Cl)_2$, is deposited from a chloroform solution of the β-chloride, containing iodine, as a reddish-yellow, crystalline powder insoluble in ether; it crystallises in large, hexagonal tables.

Platosobenzylsulphine chloride, $Pt(S(C_7H_7)_2Cl)_2$, forms greenish-yellow crystals containing 1 mol. of chloroform; it melts at 159°. The *bromide* crystallises from mixed chloroform and alcohol in crystals containing 1 mol. of chloroform and 1 mol. of alcohol; it melts at 139°. The *iodide* forms red, oblique, four-sided prisms melting at 129°. The *basic nitrate*, *nitrite*, and *sulphate* are described.

Platinibenzylsulphine chloride, $PtCl_2(S(C_7H_7)_2Cl)_2$, forms bright yellow prisms melting at 172° with decomposition. A. G. B.

Metallic Diamine Compounds. By S. M. Jörgensen (*J. pr. Chem.* [2], **39**, 1—26. See p. 351).

Determination of the Molecular Weight of Paraformaldehyde by Raoult's Method. By B. Tollens and F. Mayer (*Ber.*, **21**, 3503—3507).—Solutions of formaldehyde prepared from oxymethylene were kept in closed tubes for six months, and the molecular weight again determined with the same results as before (Abstr., 1888, 809), so that there had been no polymerisation in this time.

Paraformaldehyde, $(CH_2O)_2$, separates as a soft substance when a solution of formaldehyde is evaporated over sulphuric acid; it is readily soluble in water. The molecular weight was determined by Raoult's method. When the concentrated solution is diluted with water, formaldehyde is again formed.

Metaformaldehyde, or oxymethylene, has probably the formula $(CH_2O)_3$. The compound was previously shown to melt at temperatures varying from 142° to 171° (Abstr., 1884, 293); when freshly prepared and not sublimed, it melts gradually at 100°.

N. H. M.

Triazo-derivatives. By T. Curtius and J. Lang (*J. pr. Chem.* [2], **38**, 531—558).—The new azo-acid obtained by the action of hot concentrated aqueous alkali on ethyl diazoacetate (Abstr., 1887, 715) is *triazoacetic acid*, $C_3H_3N_6(COOH)_3$. It is best prepared as follows:—An aqueous solution of sodium hydroxide (80 grams in 120 c.c.) is heated on the water-bath and ethyl diazoacetate (50 grams) added by degrees, with continual shaking; the action soon becomes violent, and further heating is unnecessary. The half-solid contents of the flask are washed by decantation with 95 per cent. alcohol, then with absolute alcohol, and finally with ether. The sodium salt thus obtained is a bright yellow, hygroscopic powder consisting of minute needles; the yield is 55—60 grams. The *free acid* crystallises with 3 mols. H_2O in small, deep orange-red, four-sided, acute-angled, biaxial tables. It is insoluble in cold, easily soluble with partial decomposition in hot water, very easily soluble in cold absolute alcohol, gradually decomposed by hot alcohol, soluble in cold acetone and glacial acetic acid, but insoluble in the other usual solvents. When rapidly heated in a sealed tube, it decomposes at 149°, melts at 152°, and evolves carbonic anhydride at 155°; it decomposes when long heated at 60°, and this prevents a direct determination of its water of crystallisation. Heated on platinum-foil, it explodes like gunpowder, with formation of hydrogen cyanide. Nitric acid turns it red, and it reduces Fehling's solution slowly when boiled with it. The acid may also be obtained crystallised with 2 mols. H_2O in lustrous, golden laminæ.

The *potassium, sodium, silver, copper, manganese, lead, bismuth,* and *barium* salts are described. The *ammonium* salt crystallises in long orange-yellow needles easily soluble in water, and melting at 222°.

Ethyl triazoacetate, $C_3H_3N_6(COOEt)_3$, crystallises in large, ruddy, monosymmetric prisms, $a : b : c = 1{\cdot}2017 : 1 : 1{\cdot}3614$; $\beta = 73° 45'$; readily soluble in hot ether and cold alcohol, sparingly in cold ether and cold water; it melts at 110° without decomposition, sublimes in a sealed tube, and distils with partial decomposition under diminished pressure at about 270°. Its molecular weight has been determined by Raoult's method in a benzene solution.

The *methyl* salt forms small, striated, rectangular, biaxial, brick-red tables; it melts at 167—168° without decomposition, and sublimes, but cannot be distilled. The *isopropyl* salt has been obtained.

Triazoacetamide, $C_3H_3N_6(CONH_2)_3$, is obtained either as a bright yellow crystalline powder, or in golden-yellow, unsymmetrical laminæ, which melt above 300°, are insoluble in water and dilute acids, and cannot be recrystallised.

Triazimidoacetamide, $C_3HN_4(NH)_2(CONH_2)_3$, and its salts, have been described before under the name pseudo-diazoacetamide (Abstr., 1885, 884).

When heated at 100° for many hours, the yellow triazoacetic acid loses water (2 mols.) and carbonic anhydride (3 mols.), leaving a residue of *trimethintriazimide* which is soluble in absolute alcohol, and separates from the solution on the addition of ether in colourless prisms. The formula of this substance, determined by Raoult's method in an aqueous solution, is $C_3N_6H_6$. It melts at 78°, and is not decomposed at 180°; it is extremely hygroscopic, easily soluble in warm absolute alcohol, insoluble in benzene, ether, and chloroform; it is acid to blue litmus, colours Fehling's solution green, and does not evolve ammonia when heated with weak soda. Strong alkalis decompose it with formation of hydrogen cyanide and ammonia. A *silver compound*, $C_3H_6N_6,2AgNO_3$, and a *mercury compound*, $C_3H_6N_6,3HgCl_2$, have been prepared.

By heating potassium triazoacetate with aqueous potash (1 : 1) till it is dissolved, and then adding alcohol, an oil is precipitated; when this is neutralised with sulphuric acid, a white substance, of the formula

$C_3H_4N_6(COOH)_2$, is precipitated; it is equally soluble in dilute acids and alkalis, and is sparingly soluble in hot water, from which it partially crystallises on cooling as minute, lævorotatory tables, pointed at both ends; it melts at 170°. It does not evolve ammonia when heated with alkalis. When heated for some time at its melting point, it loses carbonic anhydride, leaving a residue which crystallises from water in beautiful, unsymmetrical stellate groups, and melts at 145°; its *silver nitrate compound* has the formula $C_3H_6N_6,2AgNO_3$, so that it is isomeric with the residue obtained by heating triazoacetic acid.

An aqueous solution of sodium triazoacetate decomposes after a time, and if then acidified and distilled, a strongly alkaline liquid goes over, which gives a white *silver compound*, of the formula $(CN_2Ag_2)_x$, in small, unsymmetrical crystals; the *mercurochloride* has the formula $C_3H_6N_6,HgCl_2$, so it would appear that there is yet a third isomeride of the formula $C_3H_6N_6$.

Aqueous solutions of triazoacetic acid compounds become coloured a beautiful red on exposure to the air, and its derivatives are all reddened by nitric acid or its vapour. By passing nitrous anhydride through a solution of sodium triazoacetate at 0°, unsymmetrical, carmine-coloured laminæ are precipitated; they are stable in air, and yield a red vapour when heated, which condenses again in red crystals; the formula of this substance is $C_3H_3N_6O_3(COOH)_3$.

A. G. B.

Action of Finely-divided Silver on Ethyl Bromopropionate.

By C. Hell and M. Rothberg (*Ber.*, **22**, 60—66; compare Hell and Mayer, next page).—Ethyl α-bromopropionate is heated at 150—160° for several hours with an equal weight of finely-divided silver, the whole being constantly shaken; after separating the product from the silver bromide, the following compounds can be isolated by repeated fractional distillation. (1.) A considerable portion boiling at 95—110°, which consists chiefly of ethyl propionate mixed with an unsaturated compound, probably ethyl acrylate. (2.) A large portion boiling between 110° and 200°, from which by repeated fractional distillation, a considerable quantity of ethyl α-bromopropionate was isolated. (3.) A considerable fraction boiling at 225—235°, which, on hydrolysis, yielded a mixture of the two isomeric dimethylsuccinic acids, together with a small quantity of pyrocinchonic anhydride. (4.) A considerable fraction boiling at 240—250°; this portion, on hydrolysis, yielded pyrocinchonic anhydride, dimethylsuccinic acid (m. p. 119—120°), and a small quantity of the isomeric acid (m. p. 193°). (5.) A considerable portion boiling above 250°, from which a brown syrupy acid, most probably a polymeric acrylic acid, was obtained in an impure state.

Bromine has no action on the two isomeric dimethylsuccinic acids, but in presence of phosphorus, both acids yield one and the same monobromo-substitution product. This compound crystallises from water in needles, melts at 91°, and is readily soluble in alcohol, ether, and hot water, but only sparingly in cold water. When reduced with hydrochloric acid and zinc, from whichever acid it has been prepared, it is converted into dimethylsuccinic acid (m. p. 120°).

F. S. K.

Derivatives of Phenyl-αβ-Dibromisobutyric Acid. By T. Körner (*Chem. Centr.*, 1888, 1434—1435).—*Phenyl-α-methyl-β-bromacrylic acid*, $C_{10}H_9BrO_2$, melting at 124°, is prepared by heating the alcoholic solution of phenyldibromisobutyric acid with potash at 60°. By heating it with water, carbonic anhydride is eliminated, and *phenyl-β-bromopropylene*, C_9H_9Br, and *phenyl-α-hydroxy-β-bromisobutyric acid*, $C_{10}H_{12}BrO_3$, melting at 148° are formed. Phenylbrompropylene boils at 226°, being partly decomposed thereby with evolution of hydrogen bromide; it has a fruity smell. It is also formed by decomposing phenyldibromisobutyric acid with steam. With bromine, it appears to form a tribromide. *Phenylallylene*, C_9H_8, a disagreeable-smelling, colourless oil, boiling at 185°, is formed when phenylbromopropylene is heated with alcoholic potash at 100°. *Phenylallylene dibromide*, $C_9H_8Br_2$, boils at 250—255°; the *tetrabromide* boils at 75°.

The characteristic property of the hydrocarbons of the acetylene series is the formation of additive compounds with mercury salts, and not necessarily the formation of explosive silver and cuprous compounds.
J. W. L.

Action of Sodium on Ethyl Isobutyrate. By A. Hantzsch (*Annalen*, **249**, 54—65).—Brüggemann denies the accuracy of Wohlbrück's experiments (Abstr., 1887, 1099) on the action of sodium on ethyl isobutyrate. Brüggemann states (Abstr., 1888, 1176) that no acids containing 3 atoms of oxygen are produced, and that the acids formed contain only two oxygen-atoms, and are derivatives of isobutyric acid. The author has repeated these experiments, and finds that the chief product of the reaction is *hydroxycaprylic acid*, $C_8H_{16}O_3$, as stated by Wohlbrück. In the first place, 2 mols. of ethyl isobutyrate undergo condensation in the presence of sodium, forming the compound $CHMe_2\cdot C(OH)(OEt)\cdot CMe_2\cdot COOEt$, which cannot be isolated. This is reduced by the sodium, yielding *ethyl ethoxycaprylate*, $CHMe_2\cdot CH(OEt)\cdot CMe_2\cdot COOEt$, described by Wohlbrück as ethyl dimethylisobutyrylacetate. A portion of the ethoxycaprylate is at the same time saponified, yielding hydroxycaprylic acid, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOH$. The compound obtained by acting on ethyl isovalerate with sodium, and described by Wohlbrück as ethyl isopropylisovalerylacetate, is really *ethyl ethoxycaprate*, $C_4H_9\cdot CH(OEt)\cdot CHPr\cdot COOEt$. It is decomposed by boiling with alcoholic potassium hydroxide, yielding hydroxycapric acid,

$$C_4H_9\cdot CH(OH)\cdot CHPr\cdot COOH.$$

W. C. W.

Action of Finely-divided Silver on Ethyl Bromisovalerate. By C. Hell and W. Mayer (*Ber.*, **22**, 48—60).—When ethyl bromisovalerate is treated with an equal weight of finely-divided silver at the ordinary temperature, much heat is developed; the reaction can be brought to an end by heating the mixture at 150° for about four hours, with constant shaking. The product can be separated by repeated fractional distillation into (1) a small quantity of ethyl bromide; (2) a very large quantity of ethyl valerate; (3) a small quantity of an ethereal salt boiling at 140—150°; and (4) a large portion boiling above 250°.

The fraction boiling at 140—150° yields, on hydrolysis, a viscid acid, probably dimethylacrylic acid, boiling at 180—185°, and having a pungent smell; on treating this acid with bromine in chloroform solution, there is considerable development of heat, and an impure compound, probably dibromovaleric acid, is obtained.

The portion boiling above 250° can be separated into two fractions by distilling under reduced pressure: the one boils under the ordinary pressure at 260—270°, the other at 280—300° with partial decomposition. The lower boiling fraction yields on hydrolysis two isomeric acids which can be separated by distilling with steam, but part of the ethereal salt remains unchanged; when this portion is heated at 120° with concentrated hydrobromic acid, it yields ethyl bromide and a mixture of the same two isomeric acids. The higher boiling fraction, on hydrolysis, gives a syrupy acid, from which only very small quantities of the two isomeric acids can be isolated.

Diisopropylsuccinic acid, COOH·CHPr·CHPr·COOH (m. p. 167—168°), is volatile with steam, and when separated by distillation with steam from the mixture of isomeric acids referred to above, is obtained as a colourless oil, which is probably the anhydride. The pure acid, prepared by decomposing one of the salts, separates from hot water in dendritic crystals, and melts at 167—168° when heated quickly. When heated at 150—160° in large quantities, it is converted into an oily anhydride. It is readily soluble in ether, alcohol, and chloroform, and moderately so in benzene and hot water, but only sparingly in cold water. The *sodium* salt is crystalline, and is readily soluble in water. The *barium* salt, $C_{10}H_{16}O_4Ba + 5H_2O$, *strontium* salt ($+ 3H_2O$), and *calcium* salt ($+ 4H_2O$) are crystalline, and lose the whole of their water at 120°. The *magnesium* salt, *manganese* salt, and *cobalt* salt crystallise with 7 mols. H_2O, the *nickel* salt with 5 mols. H_2O, the *cadmium* salt with 4 mols. H_2O, and the *copper* salt with 1 mol. H_2O. The *zinc*, *lead*, and *silver* salts are anhydrous, and very sparingly soluble in water.

Diisopropylsuccinic acid (m. p. 199—200°) remains when the isomeric acid (see above) is distilled with steam, and separates in granular crystals on evaporating the solution. It is readily soluble in alcohol and chloroform, and moderately so in hot water and benzene, but only sparingly in cold water. It melts at 199—200°, and sublimes in needles when heated at 210°, but does not form an anhydride. When treated with potassium permanganate in neutral aqueous solution, it is converted into an acid, probably acetic acid. The *barium* salt ($+ 2H_2O$), the *strontium* salt ($+ 4H_2O$), and the *calcium* salt ($+ 2H_2O$) are crystalline, and lose their water at 120°. The *magnesium* salt ($+ 5H_2O$), *manganese* salt ($+ 3H_2O$), *nickel* salt ($+ 4H_2O$), *copper* salt ($+ 3H_2O$), *cadmium* salt ($+ 3H_2O$), and the anhydrous and very sparingly soluble *zinc*, *copper*, *lead*, and *silver* salts were also prepared.

The syrupy acid obtained from the fraction boiling at 280—300° is separated from small quantities of the two diisopropylsuccinic acids by distilling with steam, and keeping for a long time until the non-volatile acid separates. By repeatedly extracting with water it is separated into a readily soluble, only slightly coloured acid, and a very sparingly soluble, brownish, resinous acid, both of which are readily soluble in alkalis. The former was obtained in a pure state by means of the readily soluble, crystalline *calcium* salt. Its empirical composition is $C_5H_8O_2$, and it is probably a dipolymeric dimethylacrylic acid. The more sparingly soluble acid is probably a tripolymeric dimethylacrylic acid. Neither acid combines with bromine in chloroform solution, but they both (?) yield considerable quantities of valeric acid, acetic acid, carbonic anhydride, and a small quantity of a crystalline acid, probably diisopropylsuccinic acid (m. p. 167—168°) when treated with potassium permanganate.

These results show that the action of finely divided silver on ethyl bromovalerate is analogous to the action of silver on ethyl bromobutyrate. (Compare Hell and Mülhäuser, Abstr., 1880, 542.) F. S. K.

Oxidation of Angelic and Tiglic Acids by Potassium Permanganate. By I. KONDAKOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 523—524).—The oxidation was carried on by Wagner's method (Abstr, 1888, 665), which consists in adding to a 1 per cent. solution of the potassium salt of the acid under investigation drop by drop, with continual agitation, a solution containing 1 per cent. of permanganate. The quantity of permanganate taken contained 1 atom of oxygen for 1 mol. of the acid. After separating the manganese dioxide by filtration, the liquid was submitted to distillation to remove the volatile neutral products, and the distillate which usually contains aldehyde, was treated with moist silver oxide. The silver salts were converted into sodium salts, and these on fractional distillation with sulphuric acid yielded the free acids; the acids in the different fractions were again converted into silver salts. The analysis of these proved that tiglic acid, on oxidation, yields acetaldehyde, together with some propaldehyde, whereas angelic acid yields propaldehyde as the chief, and acetaldehyde as a subsidiary product. This the author explains by the inefficiency of Kopp's method for the complete separation of angelic acid from tiglic acid. The aqueous residues left on distillation were saturated with carbonic anhydride and evaporated to dryness, and the product extracted with ether in the presence of a little dilute sulphuric acid. The analysis of silver salts prepared from the acid residue proved that tiglic acid yields acetic, angelic, and propionic acids. The investigation of the non-volatile acids has shown that angelic acid yields dihydroxyvaleric and ethyltartronic acids, and that tiglic acid yields dihydroxyvaleric acid together with the first isomeride. B. B.

Olive Oil. By K. HAZURA and A. GRÜSSNER (*Monatsh.*, **9**, 944—946; compare Abstr., 1886, 140; 1887, 359, 798, 913; and 1888, 816, 1269).—Earlier investigations of the authors have made it appear probable that the liquid portion of the fatty acids derived from olive oil consists of a mixture of two or more unsaturated acids. This view is confirmed by its iodine number.

According to Schädler, olive oil consists of a mixture of 72 per cent. of trioleïn with 28 per cent. of palmitin, stearin, and arachin; but its high iodine number points to the conclusion that the portion previously supposed to consist entirely of trioleïn contains an acid having a higher iodine number than oleïc acid. The authors now show that a mixture of hydroxystearic, $C_{18}H_{34}(OH)_2O_2$, and sativic, $C_{18}H_{32}(OH)_4O_2$, acids is formed when the liquid fatty acids of olive oil are oxidised with permanganate. It therefore follows that both oleïc and linoleïc acids are present in olive oil, and in all probability they exist in most non-drying oils. G. T. M.

Oxidation of Unsaturated Fatty Acids by Permanganate. By K. HAZURA and A. GRÜSSNER (*Monatsh.*, **9**, 947—955; compare Abstr., 1886, 140; 1888, 1270).—The authors have oxidised erucic, undecylenic, and stearolic acids with permanganate, in order to ascertain whether these substances yield oxidation products in accordance with the rule laid down by Hazura, "that unsaturated fatty acids, on oxidation with alkaline permanganate, take up as many hydroxyl-groups as they have free valencies, and are thereby converted into hydroxy-derivatives of saturated fatty acids." Under such circumstances they find that erucic acid, $C_{22}H_{42}O_2$, gives *dihydroxybehenic acid*, $C_{22}H_{42}O_2(OH)_2$. This substance is insoluble in water and ether, is only slightly soluble in chloroform, benzene, toluene, and acetic acid, and crystallises from alcohol in rhombic plates melting at 132—133°. The potassium and sodium salts are only slightly soluble in water; the salts of the alkalis and heavy metals are insoluble.

Undecylenic acid, $C_{11}H_{20}O_2$, is converted on oxidation into *dihydroxyundecylic acid*, $C_{11}H_{20}O_2(OH)_2$, crystallising in small, anhydrous needles melting at 85—86°. The acid is monobasic, and dissolves readily in alcohol, hot water, and acetic acid, but is only slightly soluble in ether and cold benzene. The potassium, sodium, barium, calcium, and magnesium salts are all soluble in water; the salts of the heavy metals are, on the other hand, insoluble.

Stearolic acid, $C_{18}H_{32}O_2$, on oxidation is converted chiefly into stearoxylic acid, $C_{18}H_{32}O_4$, which crystallises in yellow, glistening needles melting at 84—86°. At the same time a small quantity of suberic acid, $C_8H_{14}O_4$, crystallising in white needles melting at 139—140°, is formed. G. T. M.

Action of Ethyl Chlorocarbonate on Ethyl Sodacetoacetate and Ethyl Sodomalonate. By L. CLAISSEN (*Ber.*, **21**, 3567).—Vapour-density and molecular weight determinations made with the compounds obtained by Conrad and Guthzeit by the action of ethyl chlorocarbonate on ethyl sodacetoacetate and ethyl sodomalonate establish the correctness of the formulæ originally ascribed to them (*Annalen*, **214**, 31). N. H. M.

Bromazelaïc and Hydroxyazelaïc Acids. By A. BUJARD and C. HELL (*Ber.*, **22**, 68—73; compare Gantter and Hell, Abstr., 1881, 891).—Bromine has very little action on azelaïc acid at 100°, but in presence of a small quantity (0·1 per cent.) of amorphous phosphorus, the action is at an end in three hours at 100°. A mixture of dibrom- and brom-azelaïc acids is thus obtained, the latter being formed in the larger quantity, but the two products cannot be separated.

Hydroxyazelaïc acid, $OH\cdot C_7H_{13}\cdot COOH$, is prepared by boiling the mixture of brom-acids for a long time with excess of soda. The concentrated and acidified solution is shaken with ether to remove azelaïc acid, then neutralised with ammonia, copper sulphate added, and the copper salt decomposed with hydrogen sulphide. It can also be separated from the azelaïc acid by repeatedly evaporating a solution of the two ammonium salts, when ammonium azelate is decomposed, and the free acid can be separated from the more soluble unchanged salt of hydroxyazelaïc acid. Hydroxyazelaïc acid can also be purified by converting it into the zinc salt and decomposing the latter with dilute sulphuric acid. It separates from water or ether in colourless, nodular crystals, melts at 91°, and is very readily soluble in alcohol and water, but more sparingly in ether. A yellowish, viscid anhydride, $C_{18}H_{30}O_9$, is obtained when the acid is heated at 100°, or when the zinc salt is decomposed with concentrated sulphuric acid. It is reconverted into the acid when boiled with a large quantity of water. The *barium* salt, $C_9H_{14}O_5Ba + \frac{1}{2}H_2O$, the *calcium* salt ($+ 1H_2O$), and the *strontium* salt ($+ 1\frac{1}{2}H_2O$) are moderately soluble in water. The *magnesium, zinc*, and *cadmium* salts crystallise with 2 mols. H_2O. The *copper* salt ($+ 1\frac{1}{2}H_2O$), the *lead* salt ($+\frac{1}{2}H_2O$), and the anhydrous *silver* salt were also prepared. F. S. K.

Action of Ethyl Dibromosuccinate, Bromomaleate (or Fumarate), and Tartrate on Potassium Ethoxide. By E. Mulder and C. Wellemann (*Rec. Trav. Chim.*, 7, 334—340).—Analyses are given of the products of the reaction of ethyl dibromosuccinate and bromomaleate (or fumarate) with potassium ethoxide when mixed either in molecular proportion or 1 mol. of the former to 2 mols. of the latter. The product of the action of the dibromosuccinate on the ethoxide (2 mols.) gives on extracting with ether a substance that forms a compound with silver. Ethyl tartrate and potassium ethoxide form different compounds according as the reaction takes place in the cold or with heating. H. C.

Diazosuccinic, Diazosuccinamic, and Diazopropionic Acids. By T. Curtius and F. Koch (*J. pr. Chem.* [2], 38, 472—490).—This paper is mainly a continuation of a summary of the authors' previous work on the subject (compare Abstr., 1885, 885, and 1887, 33).

By the action of zinc and glacial acetic acid, diazosuccinic acid is split up into ammonia and aspartic acid. Copper aspartate crystallises with 3 mols. H_2O; Ritthausen obtained it with $4\frac{1}{2}$ mols. H_2O.

Ethyl amidopropionate hydrochloride forms groups of crystals which melt at 64—68°. When it is treated with nitrous acid, a yellow oil is obtained, which behaves like an ethyl salt of a diazo-fatty acid, and probably contains ethyl diazopropionate. *Ethyl dihydroxypropionate*, $O[CMe(OH)\cdot COOEt]_2$, distils from this oil between 80° and 86° (120 mm. pressure) as a colourless, refractive, neutral liquid, of a peculiarly penetrating odour; it gives a freely soluble *barium salt*. The rest (one-third) of the oil distils between 120° and 150°, giving an oil which solidifies, forming colourless, lustrous prisms of *ethyl azoxypropionate*, $ON_2(CHMe\cdot COOEt)_2$. This substance is neutral, melts at 95°, and is soluble in ether and alcohol; its *barium salt* is pulverulent and sparingly soluble. A. G. B.

Action of Potassium Cyanide on α-Brominated or α-Chlorinated Fatty Ethereal Salts. By N. ZELINSKY and A. BITSCHICHIN (*Ber.*, **21**, 3398—3401).—Ethyl cyanosuccinate is formed, together with ethyl α-cyanoacetate, when ethyl α-bromacetate is treated with potassium cyanide in alcoholic solution (compare Zelinsky, this vol., p. 122, and Haller, Abstr., 1888, 937). It is a heavy liquid, boils at 280—290° with only slight decomposition, and is insoluble in water. On hydrolysis with hydrochloric acid, it is converted into succinic acid.

Ethyl diethylcyanosuccinate, COOEt·C(CN)Et·CHEt·COOEt, is obtained, together with ethyl α-cyanobutyrate, by treating ethyl α-bromobutyrate in like manner, or by the action of ethyl sodocyanobutyrate on ethyl α-bromobutyrate. It is a heavy liquid, boils at 280—286°, and when hydrolysed with hydrochloric acid yields the two isomeric diethylsuccinic acids, melting at 191° and 126—127° respectively.

These experiments seem to show that the formation of such condensation products as those described above by the action of potassium cyanide on the ethereal salt of an α-brominated or α-chlorinated fatty acid is a general reaction. F. S. K.

Symmetrical Diethylsuccinic Acids. By C. HELL (*Ber.*, **22**, 67).—The author points out that he has already described the properties of the two isomeric diethylsuccinic acids (compare Hell and Mülhäuser, Abstr., 1880, 542—543). F. S. K.

Isomalic Acid. By W. OSTWALD (*Ber.*, **21**, 3534—3537).—Determinations of the molecular conductivity (Abstr., 1888, 331) of a preparation of isomalic acid made by Kämmerer (*Annalen*, **139**, 257) showed that this acid is identical with citric acid.

N. H. M.

Action of Ethyl Chlorocarbonate on the Sodium-derivatives of Acetylacetone, Ethyl Acetoacetate, and Ethyl Malonate. By L. CLAISEN and W. ZEDEL (*Ber.*, **21**, 3397—3398).—*Ethyl acetylacetonedicarboxylate*, $C(COMe)_2(COOEt)_2$, is obtained when sodacetylacetone is treated with ethyl chlorocarbonate. When ethyl sodacetoacetate is treated in like manner, the compound $COMe·C(COOEt)_3$ is formed (compare Ehrlich, *Ber.*, **7**, 892; Conrad and Guthzeit, Abstr., 1883, 45; and Michael, Abstr., 1888, 1054). The compound described as ethyl methenyltricarboxylate (Conrad and Guthzeit, *loc. cit.*) seems to be ethyl methanetetracarboxylate, $C(COOEt)_4$. F. S. K.

Glycuronic Acid. By H. THIERFELDER (*Zeit. physiol. Chem.*, **13**, 275—284; compare Abstr., 1887, 717).—An attempt to prepare a benzoyl-derivative of glycuronic acid by the method adopted by Baumann (Abstr., 1887, 228) in the preparation of tetrabenzoyldextrose, gave only a small precipitate; a better result was obtained by shaking together a mixture of substances present in the proportion of 1 mol.

of glycuronic acid, 9 mols. of benzoic chloride, and 12 mols. of sodium hydroxide (in a 10 per cent. solution); the resulting precipitate was viscous; it was dried over sulphuric acid, and freed from adherent benzoic acid by light petroleum, and from sodium benzoate and chloride by water. The substance prepared in this way dissolves readily in alcohol, especially hot alcohol. It melts at 107°; it reduces Fehling's solution. Elementary analysis gave results which correspond with the formula $C_6H_8O_7Bz_2$.

Glycuronic anhydride reacts very vigorously with aniline; better results are obtained by using potassium glycuronate dissolved in 85—90 per cent. alcohol. The crystalline compound obtained has the formula $NPh\colon C_6H_9O_6K$, it thus corresponds exactly with Sorokin's anilide of dextrose (Abstr., 1886, 526, 683; 1888, 807). It is easily soluble in water, sparingly soluble in alcohol and in ether, melts at 177°, becoming dark coloured; its solutions reduce Fehling's solution, are lævorotatory, and in the air become dark coloured, losing much of their action on polarised light.

A compound with toluylenediamine, $C_7H_6(N\colon C_6H_9O_6K)_2$, was also prepared; this corresponds to the similar compound with dextrose, prepared by Hinsberg (Abstr., 1888, 476).

The action of potassium hydroxide solutions of various strengths at different temperatures was then investigated. Oxalic acid was found in all cases. Catechol was also present, especially when strong alkali was used, and in this case a certain amount of protocatechuic acid was also formed.

The effect of putrefaction was investigated by Hoppe-Seyler's method; mud and chalk were added to the substance, and the resulting gases were analysed from time to time. The following formulæ represent the different stages in the process, as denoted by the gases formed :—(1.) $(C_6H_9O_7)_2Ca + CaCO_3 = (C_2H_3O_2)_2Ca + (C_3H_5O_3)_2Ca + 3CO_2 + H_2O$; (2.) $(C_3H_5O_3)_2Ca + 2H_2O = (C_2H_3O_2)_2Ca + 2CO_2 + 4H_2$; (3.) $(C_2H_3O_2)_2Ca + H_2O = CO_2 + CaCO_3 + 2CH_4$.

W. D. H.

Change in the Rotatory Power of Tartaric Acid in Mixed Solutions. By R. Přibram (*Ber.*, 22, 6—11).—The author has previously shown (Abstr., 1888, 1229) that the rotatory power of solutions of tartaric acid is altered considerably by various optically inactive substances, and that in many cases the rotation may be completely prevented, or even changed in direction.

When tartaric acid (5 grams) is dissolved in ethyl alcohol (20 c.c.) and the solution mixed with an equal volume of benzene, toluene, xylene, or cymene, the angle of rotation ($l = 2$ dm.) is $-0·411$, $-0·619$, $-0·652$, and $-0·791$ respectively, whereas when alcohol alone (40 c.c.) is present the angle of rotation is $+0·379$.

Chlorinated and brominated derivatives of aromatic hydrocarbons have a similar and a more marked effect, but the influence of nitro-compounds is not so great, as is shown by the following table :—

2 grams of tartaric acid contained in	In 100 c.c. of solution.		Observed angle of rotation α^{20}_{D}.
	Inactive substance.	Tartaric acid.	
	c.c.	grams.	
40 c.c. ethyl alcohol	0	5	+0·379
20 c.c. ethyl alcohol + 20 c.c. benzene .	50	5	−0·411
20 c.c. ethyl alcohol + 20 c.c. nitrobenzene	50	5	+0·317
20 c.c. ethyl alcohol + 20 c.c. toluene..	50	5	−0·619
20 c.c. ethyl alcohol + 20 c.c. nitrotoluene	50	5	−0·069
20 c.c. ethyl alcohol + 20 c.c. chlorobenzene	50	5	−0·809
20 c.c. ethyl alcohol + 20 c.c. ethyl bromide	50	5	−0·362
20 c.c. ethyl alcohol + 20 c.c. nitroethane	50	5	+0·309

Substances containing the amido-group, such as glycocine, alanine, carbamide, and aniline, increase the dextrorotatory power. In the case of carbamide, the specific rotatory power is expressed approximately by the formula $[\alpha]_D = 2·582 + 0·0515x + 0·0002313x^2$, where x = the percentage of carbamide in a solution containing 9·389 per cent. of tartaric acid.

The specific rotatory power of a solution containing 10 per cent. of tartaric acid and 4 per cent. of pyridine is $[\alpha]_D = 24·85°$, that of a solution containing 50 per cent. of pyridine and 10 per cent. of tartaric acid is $[\alpha]_D = 50·28°$, whilst that of a 10 per cent. solution of tartaric acid alone is 13·12° under the same conditions.

In a second series of experiments with solutions containing 4·8662 per cent. of tartaric acid ($[\alpha]_D = 14·405°$), it was found that the specific rotatory power is increased to 45·888, 48·950, and 49·484 by adding 25, 50, and 55 per cent. of pyridine respectively; but that on adding 60, 75, and 100 per cent. of pyridine the specific rotatory power falls to 48·364, 41·778, and 18·957 respectively (compare Thomson, Abstr., 1886, 925, and *J. pr. Chem.* [2], **35**, 145).

The results hitherto obtained show that all substances which form salts with tartaric acid increase the specific rotatory power of solutions of this acid, but in all other cases the rotatory power is decreased, and in some cases actually reversed. The fact that the decrease in the rotatory power of tartaric acid produced by members of a homologous series is, within certain limits, dependent on the molecular weight of these substances, seems to show that this phenomenon is the result of some mass-action of the molecules (compare Landolt, *Optisches Drehungsvermögen*, 1879, 59, and van't Hoff, *Études de Dynamique Chimique*, 34—42). In those cases where the change in rotatory power reaches a maximum and then decreases, it may be assumed that up to the point of maximum rotation a salt is produced, and that the subsequent decrease is caused by some mass-action of the free inactive molecules of the salt thus produced.

F. S. K.

Polarisation of Tartrate Solutions. By J. H. Long (*Amer. J. Sci.*, **36**, 351—358).—All these observations were made in a new model Laurent instrument at 20°, and with a 200 mm. tube. A solution containing 15 grams of tartaric acid in 100 c.c. of water showed a specific rotation $[\alpha]_D = 13·03$; this was diminished by free mineral acids, and also by certain neutral salts: thus with 15 grams of tartaric acid and 8 grams of sodium chloride, $[\alpha]_D = 6·16$. Rochelle salt has a rotation of 22·1; this is decreased by sodium, lithium, and thallium salts, the decrease being greater as the amount of sodium salt increases, whereas potassium and ammonium salts increase the rotation in a similar manner; calculated on the molecular proportions, the following numbers indicate the specific rotation when 1 mol. of tartrate is mixed with 1, 2, or 3 mols. of inactive salt :—

Salt.	1 mol.	2 mols.	3 mols.
$NaCl$	21·86	21·41	20·99
$NaBr$	21·79	21·42	—
$NaNO_3$	21·68	21·41	21·16
Na_2SO_4	21·32	20·49	—
$Na_2HPO_4,12H_2O$	21·40	—	—
$Na_2S_2O_3,5H_2O$	21 07	—	—
NaH_2PO_2,H_2O	21·67	20·92	—
$NaC_2H_3O_2,3H_2O$	21·72	21·16	—
KCl	22·73	22·88	23·14
KBr	22·78	23·00	—
KI	22·63	23·09	—
KNO_3	22·60	23·07	—
$KSCy$	22·52	22·66	22·82
$KC_2H_3O_2$	22·60	22·87	23 25
K_2SO_4	22·79	—	—
NH_4Cl	22·54	22·67	22·81
NH_4Br	22·54	22·70	—

The molecular rotation of the three salts, $K_2C_4H_4O_6$, $KNaC_4H_4O_6$, $Na_2C_4H_4O_6$, is respectively 64·42, 62·34, 59·85; the formation of a salt with higher or lower rotation, as the case may be, is suggested as partly explaining the above phenomenon, the cause of which, however, is still obscure.

D. A. L.

Decomposition of Amides with Alcohols. By L. Meyer (*Ber.*, **22**, 24—27).—The formation of amides and alcohols by the action of ammonia on ethereal salts is a reversible reaction, but the inverse change takes place only very partially when equivalent quantities of ammonia and ethereal salt are employed. If equilibrium is expressed thus—

p Amide + *p*′ ammonia + *q* ethereal salt + *q*′ alcohol, the reaction quotients are expressed by the formula $p'q = K^2pq'$, where K is a moderately small number. When equilibrium is established, the quantities of alcohol and amide present are, therefore, relatively large; those of ethereal salt and ammonia relatively small. The higher the temperature, the larger the quantity of ethereal salt produced, the constant K increasing as the temperature rises; in preparing amides, the temperature should therefore be kept as low as possible. K also increases as the molecular weight of the alcohol or acid radicle increases, the average value of K at 210° in reactions between ammonia and ethereal salts, formed from various acid and alcohol radicles containing an increasing number of carbon-atoms, is given in tabular form. This constant is very small in the case of secondary and tertiary alcohols.

Guldberg and Waage's law only holds good in reactions of this kind as long as the ammonia and ethereal salt are present in the proportion in which they are formed by the action of the alcohol on the amide; if either is present in excess of this quantity, the constant is changed in value.

In the case of acetamide and ethyl alcohol, $K = 0·094$; in presence of excess of ammonia it falls to 0·084, but rises to 0·134 in presence of excess of ethyl acetate. Excess of ammonia increases the formation of amide to a greater extent, and excess of ethereal salt decreases the formation of ethereal salt to a less extent than is in accordance with Guldberg and Waage's law in its usual simplest form.

In attempting to determine this relation experimentally, discordant results were obtained, when the tubes employed were slowly cooled, because, during the cooling, re-formation of amide took place. It was also found that during the reaction a considerable quantity of amine salt was produced; this salt, however, immediately decomposed, partly into water and a substituted amide, and partly into amine and ammonium salt, as shown by the following equations:— $CH_3·CONH_2 + MeOH = CH_3·COOMe + NH_3$; $CH_3·COOMe + NH_3 = CH_3·COO·NH_3Me$; $CH_3·COO·NH_3Me = CH_3·CONHMe + H_2O$; $CH_3·COO·NH_3Me + NH_3 = CH_3·COO·NH_4 + NH_2Me$. If an amine salt is present, it has no influence on the course of the reaction; acetamide is decomposed by ethyl alcohol to the same extent, whether ethylamine acetate is present or not, the amine salt being almost completely converted into ethyl acetamide.

When a few hundredths per cent. of acid are present, the formation of ethereal salt is hastened very considerably: 5 mols. of ethyl alcohol only decomposed 8·3 per cent. of pure butyramide in 24 hours; whereas in presence of 0·044 per cent. of butyric acid, 42 per cent. was decomposed in the same time, and in presence of 4·4 per cent. of acid, 44 per cent. was decomposed.

Pure acetamide is odourless, has a neutral reaction, and melts at 81—82° (see Mason, Trans., 1882, **108**). Pure propionamide melts at 79—80°, butyramide at 115°, and isobutyramide at 129°.

F. S. K.

Synthesis of the Asparagines. By A. Piutti (*Chem. Centr.*, 1888, 1459—1460).—*Ethyl β-aspartate*, $COOH·CH(NH_2)·CH_2·COOEt$, is prepared by reducing 5 grams of the oxime of ethyl oxalacetate in

50 c.c. of aqueous alcohol with acetic acid and 30 grams of sodium-amalgam (5 per cent.), the solution being retained acid by occasional addition of acetic acid; any great development of heat must also be avoided. After filtering, cupric acetate is added, and the copper salt allowed to crystallise out. The latter is anhydrous, and the determination of the copper agreed with the formula $(C_6H_{10}NO_4)_2Cu$. Precipitation of the copper in the cold with hydrogen sulphide and concentration, and ultimate crystallisation over sulphuric acid, gave the ethyl salt in leaf-like, anhydrous crystals melting at 200—201°; a small quantity of inactive aspartic acid was found in the mother-liquor.

Ethyl α-aspartate, $COOH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOEt$, is prepared by reducing 80 grams of the oxime of ethyl oxalacetate in absolute alcohol with 9 grams of sodium, in a vacuum over sulphuric acid during two to three days, whereby one ethyl-group is eliminated. The dark-yellow, gelatinous mass is dissolved in water, alcohol added until slight precipitation ensues, and then acidified with acetic acid and reduced with sodium-amalgam until ferric chloride no longer produces a violet coloration, and until cupric acetate produces a heavy precipitate. Generally 6—7 parts of the amalgam to 1 part of the oxime are sufficient. Cupric acetate is added to the filtrate, when a green or blue, crystalline precipitate soon separates; this is nearly insoluble. Precipitation with hydrogen sulphide, expulsion of the excess of the latter in a vacuum over lime, filtration and concentration at a low temperature, first in a current of air and finally over sulphuric acid in a vacuum, results in the separation of the ethyl α-salt in large crystals, in addition to a little crystalline aspartic acid. It is purified by fractional crystallisation from water and alcohol. The ethyl salt is anhydrous, melts at 165° with decomposition, is very soluble in water, but only sparingly in alcohol, insoluble in ether. It is saponified by boiling potash or hydrogen chloride, with separation of inactive aspartic acid, as in the case of the ethyl β-salt.

According to L. Brugnatelli, the crystals of the ethyl α-salt are monoclinic; $a : b : c = 1{\cdot}8822 : 1 : 1{\cdot}1883$; $\beta = 82° 15'$. The plate-like crystals showed complete cleavage in the direction (100). The plane of the optical axis is at right angles to (010). The double refraction is strong and positive. The *copper salt* of the ethyl α-salt, $(C_6H_{10}NO_4)_2Cu + 2H_2O$, crystallises in blue, flattened needle clusters which yield water and alcohol at 100°. The *hydrochloride* of the ethyl α-salt, $C_6H_{11}NO_4,HCl$, is a white, crystalline mass readily soluble in water, little soluble in alcohol. The aqueous solution of the ethyl α-salt is optically inactive.

Inactive asparagine, $COOH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CONH_2$, is prepared by heating the ethyl α-salt with alcoholic ammonia for five to six hours. The solution is concentrated at first at a low temperature, then in a vacuum, the residue dissolved in a little water, precipitated with alcohol, and recrystallised from water. Thus obtained, it forms a mass of lustrous plates containing 1 mol. H_2O, which become opalescent but do not melt at 118—120°, yellow-coloured at 200°, and are completely decomposed at 215°. α-Asparagine is readily soluble in hot water, somewhat soluble in cold water, nearly insoluble in alcohol and ether. It is acid, and liberates acetic acid from its salts. Magnesia does not decompose it, but with 30 per cent. potash, ammonia is evolved. In a vacuum, or at 100°, it loses its water of crystallisation. Addition of cupric acetate to the aqueous solution precipitates after a time the salt $(C_4H_7N_2O_3)_2Cu + 2H_2O$, in small, light blue, transparent masses of prisms. The *hydrochloride*, $C_4H_8N_2O_3,HCl$, is a crystalline, deliquescent mass. By boiling with hydrogen chloride (2 mols.) and subsequent treatment with ammonia (1 mol.), the (inactive) α-asparagine, like the two active asparagines, is changed to inactive aspartic acid.

According to L. Brugnatelli, α-asparagine crystallises in the triclinic system. $a : b : c = 1\cdot5959 : 1 : 0\cdot5668$; $\alpha = 91° 19$, $\beta = 113° 12'$, $\gamma = 83° 48'$. J. W. L.

Constitution of the Monethyl Aspartates and the Asparagines. By A. Piutti (*Chem. Centr.*, 1888, 1460).—In order to determine the constitution of the monethyl aspartates and the asparagines, the author prepared the corresponding ethyl oximidosuccinates, and compared them with the ethyl α-oximidosuccinate,

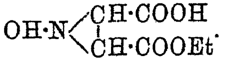
$$COOH\cdot CH_2\cdot C(NOH)\cdot COOEt,$$

of Ebert. One of these ethyl salts is prepared by treating the oxime of ethyl oxalacetate with sodium ethoxide in alcohol, evaporating the mixture in a vacuum, and decomposing the residue with the calculated quantity of sulphuric acid. The salt is reduced with sodium-amalgam in alcohol in presence of acetic acid, and the copper salt of monethyl aspartate precipitated with cupric acetate. The salt has the formula $(C_6H_{10}NO_4)_2Cu + 2H_2O$, is crystalline, insoluble in water, and from it the ethyl salt, melting at 165°, is obtained. The *ethyl oximidosuccinate* derived from this differs from that obtained by Ebert, the melting point of the former being 54·7°, that of the latter 110—111°. It crystallises in needles, is somewhat soluble in water, readily so in alcohol, ether, and chloroform, little soluble in benzene and light petroleum, and does not give ethyl α-nitrosopropionate when its solution is heated, as is the case with that of Ebert's salt. With ferric chloride, an intense violet coloration is produced.

In the solution of the ammonium salt, mercuric salts produce white precipitates, which become forthwith reduced. The barium salt is white, and crystallises from acetic acid. If melted in a vacuum or over sulphuric acid, the *anhydride* $C_6H_7NO_4$ is formed.

The *silver* salt, $C_6H_8AgNO_5$, forms needles and leaves; it is sparingly soluble in water, not affected by the light, and readily decomposed by heat. It also loses 1 mol. H_2O when heated or when placed in a vacuum over sulphuric acid. With methyl iodide, the oxime of ethyl oxalacetate is not regenerated, the *anhydride*, $C_8H_{12}NO_4$, being formed. This boils at about 160° under 40 mm. pressure. With ammonia, the *amide*, $C_6H_8N_2O_3$, melting at 166—167° is formed, whereas the oxime of ethyl oxalacetate with ammonia forms the amide, $C_4H_7N_3O_3$, melting at 184°.

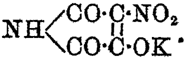
By reducing ethyl α-oximidosuccinate with 5 per cent. sodium-amalgam, inactive aspartic acid is produced in the aqueous solution, and monethyl aspartate melting at 165° in the acetic acid solution. The latter has therefore the formula $COOH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOEt$. Since the ethyl oximidosuccinate (m. p. 54·7°) also yields monethyl aspartate (m. p. 165°), it probably has the constitution



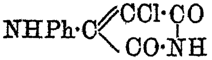
$$OH{\cdot}N\left\langle\begin{array}{l}CH{\cdot}COOH\\ \,|\\ CH{\cdot}COOEt\end{array}\right. .$$

The *inactive* asparagine obtained from the ethyl aspartate (m. p. 165°) has therefore the constitution $COOH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CONH_2$. The ethyl aspartate, melting point 200°, has accordingly the formula $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}COOEt$, and the *active* asparagine the formula $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CONH_2$. This result confirms that obtained by Guareschi (this Journal, 1876, i, 457) for the lævorotatory common asparagine, and shows that the dextrorotatory asparagine is its physical isomeride. J. W. L.

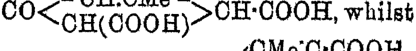
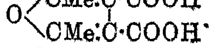
Derivatives of Maleïnimide. By G. Ciamician and P. Silber (*Ber.*, 22, 33—35).—The salt $C_4HN_2O_5K$ separates in light-yellow crystals, when a dilute alcoholic solution of dichloromaleïnimide (5 grams) is warmed with potassium nitrite (15 grams) for four hours. It is almost insoluble in cold water, explodes slightly when heated, and is converted into oxalic acid when treated with stannous chloride and hydrochloric acid. When a warm, aqueous solution is mixed with dilute sulphuric acid, the salt separates unchanged, but if the mixture is boiled for a long time, the solution becomes colourless, and oxalic acid is obtained. The constitution of this salt is probably



$$NH\left\langle\begin{array}{l}CO{\cdot}C{\cdot}NO_2\\ \quad\ \ \|\\ CO{\cdot}C{\cdot}OK\end{array}\right. .$$

The compound  $NHPh{\cdot}C\left\langle\begin{array}{l}CCl{\cdot}CO\\ \quad\quad\ |\\ \ CO{\cdot}NH\end{array}\right.$ is obtained when an alcoholic solution of the imide (3 grams) is boiled with aniline for 15 minutes. It crystallises from alcohol in yellow needles melting at 196°.

Dichloromaleïnimide also combines with phenylhydrazine in alcoholic solution, yielding an orange-red, crystalline compound. F. S. K.

Constitution of Carbopyrotritartaric Acid. By L. Knorr (*Ber.*, 22, 146—152).—According to Fittig, carbopyrotritartaric acid has the unsymmetrical formula  $CO\left\langle\begin{array}{l}-CH{:}CMe-\\ CH(COOH)\end{array}\right\rangle CH{\cdot}COOH$, whilst the author ascribes to it the constitution  $O\left\langle\begin{array}{l}CMe{:}C{\cdot}COOH\\ \quad\quad\ \ |\\ CMe{:}C{\cdot}COOH\end{array}\right.$. The correctness of this symmetrical formula is shown by the fact that the acid yields only one ethyl hydrogen salt and only one pyrotritartaric acid. (Compare next Abstract.) N. H. M.

Carbopyrotritartaric Acid. By L. Knorr and W. Cavallo (*Ber.*, 22, 153—158).—Diethyl carbopyrotritartrate (Abstr., 1885, 248) is a colourless, strongly refractive oil, boiling at 275·5° (under 735 mm. pressure). Alcoholic potash hydrolyses it readily to carbopyrotritartaric acid, whilst aqueous potash converts it into Harrow's monethyl salt. *Silver ethyl carbopyrotritartrate*, $C_{10}H_{11}AgO_3$, forms a white, voluminous precipitate; when distilled, ethyl pyrotritartrate is formed. *Dimethyl carbopyrotritartrate*. $C_{10}H_{12}O_5$, prepared by heating the di-silver salt with methyl iodide at 100°, melts at 63—64°, boils at 258° under 756 mm. pressure, dissolves readily in the usual organic solvents, very sparingly in water. Cold concentrated hydrochloric acid converts it into the *methyl hydrogen salt*, $C_9H_{10}O_5$, which melts at 129°. The *silver methyl salt*, $C_9H_9AgO_5$, was prepared. When this is distilled, *methyl pyrotritartrate*, $C_8H_{10}O_3$, is formed; it boils at 192° under 759 mm. pressure.

Methyl ethyl carbopyrotritartrate, $C_{11}H_{14}O_5$, obtained by the action of methyl iodide on the silver ethyl salt, or by the action of ethyl iodide on the silver methyl salt, boils at 268° under 756 mm. pressure; it shows a blue fluorescence. On hydrolysis with fuming hydrochloric acid, methyl hydrogen and ethyl hydrogen carbopyrotritartrates are formed. N. H. M.

Derivatives of Ethyl Diacetosuccinate. By L. KNORR (*Ber.*, **22**, 158—168).—*Ethyl isocarbopyrotritartrate*, $C_{10}H_{12}O_5$, prepared by heating pure ethyl diacetosuccinate at 170—180°, melts at 110°, and distils at 280° under 15 mm. pressure. Ethyl pyrotritartrate and diethyl carbopyrotritartrate are also formed. It crystallises from water in slender needles, very sparingly soluble in water, readily in ether, chloroform, hot alcohol, and in alkali. It reduces gold and silver solutions in the cold, and gives a blue coloration with ferric chloride. It reacts with phenylhydrazine at the ordinary temperature, yielding bis-phenylmethylpyrazolone. When heated on a water-bath with hydroxylamine, bis-phenylmethylisoxazolone, $C_8H_8N_2O_4$, is formed. This is identical with the compound previously prepared by the action of hydroxylamine on ethyl diacetosuccinate (compare *Annalen*, **236**, 298; also Münchmayer, Abstr., 1886, 877; and Meyer, *Ber.*, **21**, 1361).

Isocarbopyrotritartaric acid, $C_8H_8O_5$, is obtained by boiling the ethyl salt with 20 per cent. soda solution (8 parts) for 5—10 minutes, cooling with ice and pouring into dilute (1 : 4) sulphuric acid. It melts at 200—209° (according to the rate at which it is heated), with evolution of carbonic anhydride, and formation of two compounds melting respectively at 175° and 60°. The *barium salt*, $C_{16}H_{14}O_5Ba + 2H_2O$, separates in slender aggregates of crystals. When the acid is heated with water at 110—120°, it is converted into acetonylacetone (Paal, Abstr., 1885, 505); the decomposition takes place at 100°.

N. H. M.

Hydrolysis of Ethyl Diacetosuccinate: Acetonylacetone and Diacetosuccinic Acid. By L. KNORR (*Ber.*, **22**, 168—172).—Acetonylacetone is readily prepared by keeping ethyl diacetosuccinate with a slight excess of 30 per cent. aqueous soda for some days at the ordinary temperature. The solution is saturated with ignited potassium carbonate, when the acetonylacetone separates as an oil, which is extracted with ether and distilled. It boils at 194° (under

754 mm. pressure). Sp. gr. = 0·9955 and 0·9945, compared with water at 11·6° and 19·1°. When the solution in acetic acid is heated to boiling with phenylhydrazine, phenylamidodimethylpyrroline is formed. This melts at 90—92°, and boils at 270° (not at 170°; Abstr., 1885, 995).

Diacetosuccinic acid is obtained as follows: the ethyl salt is kept with 25 per cent. aqueous soda (5 parts) for at least eight days at the ordinary temperature; it is then acidified and extracted with ether. The oily product is dried in a vacuum, the mass of crystals thus obtained washed with ether, and then crystallised from ether. It decomposes at about 160°, is soluble in water and alcohol, sparingly soluble in ether. It gives no coloration with ferric chloride, and has no reducing properties. Boiling water has no action on it. When heated with hydrochloric acid on a water-bath, it is converted into carbopyrotritartaric acid. The *barium salt*, $C_8H_8BaO_6$, was prepared.

N. H. M.

Substituted Pyromucic Acids. By H. B. Hill and A. W. Palmer (*Amer. Chem. J.*, **10**, 409—425; compare this vol., p. 37).—The β-sulphonic acids are prepared by sulphonating δ-bromopyromucic acid.

β-Sulpho-δ-bromopyromucic Acid.—The sulphonation of δ-bromopyromucic acid proceeds regularly, and the product is purified by conversion into the acid barium salt, $Ba(C_5H_2BrSO_6)_2 + 4H_2O$, which forms large crystals, readily soluble in hot water, whilst the neutral salt, $BaC_5HBrSO_6 + 5H_2O$, is only sparingly soluble (2·68 per cent. at 20°). The free acid is crystalline, but deliquescent. The following salts are also described:—$CaC_5HBrSO_6 + 2H_2O$; $PbC_5HBrSO_6 + 1\frac{1}{2}H_2O$; $Ag_2C_5HBrSO_6 + 2H_2O$, and $K_2C_5HBrSO_6$. By treating the barium salt with bromine in the requisite quantity, the barium salt of *αα-dibromofurfuran-β-sulphonic acid*, $Ba(C_4HBr_2SO_4)_2H_2O$, is readily obtained; both it and the potassium salt, $KC_4HBr_2SO_4$, are crystalline and readily soluble; by using more bromine, or by again treating these first products, the salts of *sulphofumaric acid* are obtained; of these the barium, lead, and silver salts are very sparingly soluble in water, the potassium and calcium salts are very soluble, and neither the salts nor the free acid could be obtained in the crystalline form. Only the barium and silver salts were analysed, $Ba_3(C_4HSO_7)_2 + xH_2O$ and $Ag_3C_4HSO_7 + xH_2O$. Nitric acid also converts β-sulpho-δ-bromopyromucic acid into sulphofumaric acid, but sometimes this suffers decomposition, yielding oxalic acid. Fusion with potash gives nothing but oxalic acid. Zinc-dust and ammonia convert β-sulpho-δ-bromopyromucic acid or its barium salt into *β-sulphopyromucic acid*, which is purified by means of its acid barium salt, $Ba(C_5H_3SO_6)_2 + 3H_2O$; the salts $BaC_5H_2SO_6 + 3H_2O$, $CaC_5H_2SO_6 + 2H_2O$, and $K_2C_5H_2SO_6 + 2\frac{1}{2}H_2O$ are also described; they are all crystalline.

Attempts to prepare a γ-sulphopyromucic acid by acting with fuming sulphuric acid on β-δ-dibromopyromucic acid were of no avail, as only monobromomaleic acid is formed; and similarly tribromopyromucic acid yields only a dibromomaleic acid.

H. B.

Physical Properties of Benzene and Thiophen. By G. CIAMICIAN (*Ber.*, **22**, 27—30).—Horstmann (Abstr., 1888, 1069) has shown that the contradictory results obtained when attempts are made to deduce the constitution of benzene from a study of its physical properties, can be explained in a satisfactory manner if the formula recently advanced by Baeyer is accepted. He compared the heat of combustion of benzene with that of hexane, and found that the difference ($4H_2$) is four times as great as the difference between the heat of combustion of methane and methylene (CH_2), and is equal to 211·7 Cals. The author points out that the difference in the heat of combustion of ethyl sulphide and thiophen is equal to $3H_2$, namely, 158·8 Cals. According to R. Schiff, the molecular volume of benzene is 95·94, that of the C_4H_4-group is therefore 95·94 × $\frac{2}{3}$ = 63·96. Now since the molecular volume of thiophen is 84·93, the atomic volume of sulphur is 84·93—63·96 = 20·97, and if this value is taken instead of 22·6, as determined by H. Kopp (*Annalen*, **96**, 303), the calculated molecular volume of ethyl mercaptan, amyl mercaptan, ethyl sulphide, and methyl sulphide, are more in accordance with the observed results. Taking the value for the molecular refractive energy of benzene determined by Brühl, $p\frac{\mu_a - 1}{d} = 44·03$, and $p\frac{\mu^2_a - 1}{(\mu^2_a + 2)d} = 25·93$, and taking that of thiophen determined by Nasini, $p\frac{\mu_a - 1}{d} = 41·40$, and $p\frac{\mu^2_a - 1}{(\mu^2_a + 2)d} = 24·13$, it follows that the molecular refractive energy of the C_4H_4-group is $p\frac{\mu_a - 1}{d} = 29·39$, and $p\frac{\mu^2_a - 1}{(\mu^2_a + 2)d} = 17·28$. The atomic refractive energy of sulphur is therefore 12·04 and 6·85. The values found by Nasini being 14·10 and 7·87 in compounds containing singly-bound sulphur, and 15·61 and 9·02 in carbon bisulphide and compounds containing doubly-bound sulphur.

These considerations seem to show that the constitution of the C_4H_4-group in the thiophen molecule is similar to that of the same group in benzene.

F. S. K.

Nitration. By L. MEYER (*Ber.*, **22**, 18—23. Compare also p. 341). —The quantity of nitrobenzene formed in a given time by the action of a given volume of nitric acid on benzene is greater the less the quantity of benzene present; for example, 100 mols. of nitric acid and 100 mols. of benzene yield 17 mols. of nitrobenzene in 15 minutes at 3°; but when 300 mols. of benzene are employed, the quantity of nitrobenzene produced is 10·02, and when 700 mols. of benzene are used, only 3·6 mols. of nitrobenzene are produced in the same time under exactly similar conditions. The results are similar when small quantities of benzene mixed with a constant quantity of nitrobenzene are treated with a constant quantity of nitric acid. A mixture of 100 mols. of nitric acid and 5 mols. of benzene diluted with 100 mols. of nitrobenzene yielded 4·4 mols. of nitrobenzene in 15 minutes at 3°; as the quantity of benzene was gradually increased from 5 to 100 mols., the quantity of nitrobenzene formed in the same time and under the same conditions gradually decreased from 4·4 to 2·2 mols.

When a mixture of 100 mols. of benzene and 100 mols. of nitrobenzene is treated with quantities of nitric acid varying from 50 to 450 mols., the quantity of nitrobenzene produced in 15 minutes at 3° is proportional to the square of the quantity of the acid employed. The quantity of acid decomposed is almost proportional to the quantity added, the increase being about 2 55 per cent. on the average for every additional 50 mols. of acid. The quantity of nitrobenzene produced in 15 minutes at 3° is expressed very closely by the formula $N = 5 \cdot 1(A/B)^2 - 2 \cdot 9A/B$, where A is the number of molecules of acid, and B the number of molecules of benzene in the mixture.

Nitrobenzene retards the reaction between nitric acid and benzene far more than benzene does, and even to a greater extent than an equivalent quantity of water, but less than an equal volume of water. As soon as the volume of water produced becomes equal to that of the anhydrous acid present, the reaction ceases, so that at least 2 mols. of acid are required to nitrate 1 mol. of benzene unless sulphuric acid is also added. If the proper quantity of anhydrous acid is employed in nitrating benzene, equilibrium is established very soon even in the cold, but if the acid is not quite anhydrous, or if excess of benzene or nitrobenzene is present, hours or even days are required to complete the reaction, and in any case the nitration, which is most rapid at first, gradually decreases. For example, with a mixture of equal molecules of nitric acid, benzene, and nitrobenzene at the average temperature of 18°, the reaction was not finished until after 71 hours' time; 50 per cent. of the benzene had by this time been changed, but even then there was a slight subsequent reaction. A table is given showing the quantity of acid decomposed after various lengths of time, when quantities of benzene varying from 25 to 150 mols. are added to a mixture of 100 mols. of nitric acid and 100 mols. of nitrobenzene. The table shows that in the experiments with 25 mols. of benzene the conversion into nitrobenzene is complete in half an hour, and that then the formation of dinitrobenzene commenced. In the other experiments, the reaction proceeded at first the more quickly the smaller the quantity of benzene present, this difference gradually becoming less and less the nearer the process reached the point at which half the acid is decomposed.

F. S. K.

Orthodiethylbenzene. By A. Voswinkel (*Ber.*, **21**, 3499—3501).—*Orthodiethylbenzene*, $C_6H_4Et_2$, is prepared by the action of sodium on a well-cooled mixture of orthodichlorobenzene and ethyl bromide; in 12 hours the reaction is finished. The product is distilled and purified by conversion into the sulphonamide, &c. It is a colourless liquid, of a slightly aromatic odour, boils at 184—184·5°, and becomes viscid at −20°; sp. gr. = 0·8662 at 18° (water at 4° = 1). Aqueous alkaline permanganate solution oxidises it to orthophthalic acid. *Barium diethylbenzenesulphonate*, $(C_{10}H_{13} \cdot SO_3)_2Ba + H_2O$, crystallises in concentrically grouped prisms rather readily soluble in water; the *potassium salt* is very readily soluble in water. The *sulphonamide*, $C_{10}H_{13}\cdot SO_2NH_2$, crystallises from dilute alcohol in colourless, rhombic plates melting at 119°. *Tetrabromorthodiethylbenzene*, $C_6Et_2Br_4$, crystallises from alcohol in colourless prisms melting at 64·5°. N. H. M.

Creolin. By T. WEYL (*Ber.*, **22**, 138—139).—Two preparations known as creolin were examined, with the following result:—Artmann's creolin is a dark-brown oil of a sharp odour, which forms an emulsion with water; when cooled, crystals of naphthalene separate. It contains 84·9 per cent. of hydrocarbons, 3·4 per cent. of phenols, 1·5 per cent. of acids, and 0·8 per cent. of sodium. Pearson's creolin is easily distinguished from the above in being readily soluble in ether. It contains hydrocarbons, 56·9 per cent.; phenols, 22·6 per cent.; acids, 0·4 per cent.; and sodium, 2·4 per cent. These two preparations were used medicinally, notwithstanding that their composition or freedom from poisonous constituents was not known. N. H. M.

Metacresols. By A. CLAUS and J. HIRSCH (*J. pr. Chem.* [2], **39**, 59—64).—2 : 4 : 6-*Tribromometacresol* is formed when bromine acts on a chloroform solution of metacresol in presence of iron; it forms colourless crystals melting at 82° (uncorr.). Its *potassium* and *sodium* salts are described. The *ethyl ether* forms colourless aggregates of needles melting at 36° (uncorr.), and the *acetate* melts at 68° (uncorr.). When it is oxidised by chromic acid in strong acetic acid solution, several bromotoluquinones are formed, but in weaker acetic acid (50 per cent.) 2 : 6-*dibromotoluquinone* is obtained in lustrous, yellow crystals melting at 115° (uncorr.), soluble in ordinary solvents and distilling with steam. When reduced, it yields 2 : 6-*dibromotoluquinol*, which crystallises in small, colourless needles or large, monosymmetrical tables melting at 117° (uncorr.), and becoming brown on exposure to light.

Nitrodibromometacresol, [Br : Br = 2 : 6], obtained by acting on a cold glacial acetic acid solution of tribromometacresol with nitric acid (sp. gr. 1·4), crystallises in yellow, lustrous needles, melting with decomposition at 143° (uncorr.), insoluble in water, easily soluble in alcohol and chloroform. The *potassium* and *sodium* salts are described.

Bromometacresyl acetate is obtained by brominating metacresyl acetate as colourless, lustrous needles melting at 83° (uncorr.); it yields bromometacresol on hydrolysis.

The nitrocresol (m. p. 56°, Abstr., 1883, 662) yields a *nitrodibromocresol* which crystallises in yellow needles melting at 93° (uncorr.), whereas the nitrocresol of melting point 127° (uncorr.) yields the nitrodibromometacresol described above, so this latter nitrocresol is *paranitrometacresol*. A. G. B.

Derivatives of Hydroxyquinol. By W. SCHWEITZER (*Chem. Centr.*, 1888, 1434).—Methoxyquinone combines with aniline to form *methoxyquinone anilide*, $OMe\cdot C_6H(NHPh)_2O_2$; this dissolves in concentrated sulphuric acid to a dark-blue solution, sublimes in copper-coloured needles, and melts above the boiling temperature of sulphuric acid.

Methoxyquinone anisidide, $OMe\cdot C_6H(NH\cdot C_6H_4\cdot OMe)_2O_2$, forms purple-red needles.

Methoxyquinone orthotoluidide, $OMe\cdot C_6H(NH\cdot C_6H_4Me)_2O_2$, of a brown colour, melts at 239°; the *paratoluidide* shows the red colour of the anisidide, and the *ortho-xylidide* forms brown needles similar to the orthotoluide, and melts at 228°; the *diphenylamide*, $OMe\cdot C_6H(NPh_2)_2O_2$, forms dark-blue flakes, and melts at 120°.

Tribromomethoxyquinone, $OMe\cdot C_6Br_3O_2$, prepared by the action of bromine on methoxyquinone, melts at 169° and forms red needles. *Dinitromethoxyquinone*, $OMe\cdot C_6H(NO_2)_2O_2$, prepared by the action of nitric acid on the quinone, forms light-yellow needles melting at 213°. *Methoxyquinol*, $OMe\cdot C_6H_3(OH)_2$, melting at 194°, is prepared by reducing the quinone with sulphurous acid, and forms light-grey prisms. The presence of a methyl-group was determined by the application of Zeisel's reaction.

Trimethoxybenzene, $C_6H_3(OMe)_3$ [1 : 2 : 4], is an oil boiling at 247°. *Dinitrotrimethoxybenzene*, melting at 131°, is formed from the last-named compound, and crystallises in brownish-yellow needles. It is identical with the compound obtained from asarone by Butlerow and Rizza (Abstr., 1888, 458). J. W. L.

Products of Decomposition of Chlor-, Brom-, and Nitr-anilic Acids. By S. Levy and K. Jedlicka (*Annalen*, **249**, 66—98).—The action of bromine on chloranilic and bromanilic acids has been previously described by the authors (Abstr., 1887, 1106). When nitranilic acid is treated with chlorine or bromine, oxalic acid and chloropicrin or bromopicrin are formed. The action of chlorine on chloranilic acid has already been described (Abstr., 1888, 443).

W. C. W.

Pentamidotoluene. By A. W. Palmer (*Ber.*, **21**, 3501—3502).—*Trinitrodibromotoluene*, $C_6MeBr_2(NO_2)_3$, obtained by boiling symmetrical dibromotoluene (m. p. 39°) with a mixture of sulphuric and nitric (sp. gr. = 1·52) acids (equal vols. 20 parts), crystallises from alcohol in long, pale-yellow prisms melting at 229—230°.

Trinitrodiamidotoluene, $C_6Me(NO_2)_3(NH_2)_2$, is prepared by heating the above compound with alcoholic ammonia in a water-bath for eight hours; the product is washed with cold alcohol and crystallised from boiling alcohol. It forms small, yellow prisms melting at 222°.

Pentamidotoluene, $C_6Me(NH_2)_5$, is formed when trinitrodiamidotoluene is reduced with tin and hydrochloric acid; the tin salt is precipitated by saturating the liquid with hydrogen chloride, and is then decomposed with hydrogen sulphide. The filtrate from the tin sulphide is precipitated by passing hydrogen chloride through it, the hydrochloride washed with hydrochloric acid and ether, and dried first over soda-lime and afterwards at 100°. The *hydrochloride*, $C_6Me(NH_2)_5,3HCl$, forms white, microscopic prisms, very readily soluble in water, sparingly in alcohol; the crystals became quickly dark when exposed to air; the *sulphate* is readily soluble in water;

the *platinochloride*, $[C_6Me(NH_2)_5]_2,3H_2PtCl_6$, forms black crystals. The *picrate* forms a yellow, crystalline precipitate. N. H. M.

Metaxylylamidomethane. By W. HINRICHSEN (*Ber.*, **22**, 121—124; compare this vol., p. 131).—Dimethylbenzaldehyde (metaxylobenzaldehyde) is best prepared by oxidising the alcohol in the cold. It boils at 215—216° (not 232°), and when kept for some time in alcohol cooled to —40° solidifies to a crystalline mass, which melts at —9° to —8°. When heated with dilute nitric acid, xylylic acid is formed.

Metaxylylbenzamidomethane, $C_9H_{11}\cdot NHBz$, is obtained by treating xylylamidomethane (2 grams) with benzoic chloride (2 grams), heating the product for a short time on a water-bath, neutralising, and extracting twice with hot water. The undissolved substance is crystallised from alcohol, from which it separates in matted needles. It melts at 98°, dissolves readily in alcohol and benzene, &c., very sparingly in water

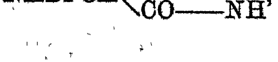
Dimethylbenzylcarbamide, $C_6H_2Me_2\cdot CH_2\cdot NH\cdot CONH_2$, is formed by the action of potassium cyanate on a concentrated aqueous solution of xylylamidomethane hydrochloride; the mixture is afterwards heated on a water-bath to finish the reaction. It crystallises from alcohol in slender needles, melts at 184·5°, and is rather sparingly soluble in water. The *thiocarbamide*, $CS(NH\cdot C_9H_{11})_2$, is prepared by adding carbon bisulphide (4·5 grams) to xylylamidomethane (10 grams), dissolved in alcohol, and heating the product for about 10 hours on a water-bath until no more carbon bisulphide is given off. It crystallises from hot alcohol in lustrous needles melting at 176—177°.

Dimethylbenzyl isothiocyanate, $CS{:}N\cdot C_9H_{11}$, was prepared by boiling the carbamide with syrupy phosphoric acid (3 parts) in a reflux apparatus. The yield was bad, and the product was not analysed.

Dimethylbenzyl acetate, $C_9H_{11}\cdot OAc$, obtained by treating metaxylyl carbinol (2 grams) with acetic chloride (4 grams), forms a clear liquid of an aromatic odour, and boils at 230—234° with slight decomposition. The *benzoate*, $C_9H_{11}\cdot OBz$, is a yellow oil boiling at 332—333°.

N. H. M.

Dibenzamidodihydroxytetrene. By L. RÜGHEIMER (*Ber.*, **22**, 114—118).—When dibenzamidodihydroxytetrene (this vol., p. 249) is boiled with water and lead carbonate, the *lead salt*, $C_{18}H_{12}N_2O_4Pb$, is formed; it is a sparingly soluble, crystalline substance. The *calcium salt*, $(C_{18}H_{13}N_2O_4)_2Ca$, crystallises in microscopic prisms, sparingly soluble in water. The normal *calcium salt*, obtained by treating the very concentrated ammoniacal solution of dibenzamidohydroxytetrene with calcium chloride, is extremely soluble in water. When a solution of dibenzamidodihydroxytetrene in methyl alcohol (10 parts) is saturated with hydrogen chloride, the compound $C_{11}H_{10}N_2O_3$ is formed. This crystallises from methyl alcohol in lustrous plates, melts at 200° with partial decomposition, and is moderately soluble in cold methyl alcohol. The compound has probably the constitution



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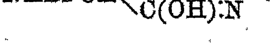

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N. H. M.

Two Isomeric Azoxytoluenes Derived from Paranitrotoluene. By J. V. Janovsky and K. Reimann (*Ber.*, 22, 40—45).—When the crude product of the action of zinc-dust and soda on pure paranitrotoluene is dissolved in a large quantity of hot, glacial acetic acid, parazotoluene (m. p. 144°) alone separates on cooling; if the mother-liquor is evaporated, a mixture of several substances is obtained, from which, by recrystallisation from alcohol, a red substance (m. p. 109—110°) very similar to azotoluene is first obtained, then an orange-yellow, crystalline substance melting at 75°, then the azoxytoluene (m. p. 70°) obtained by Melms (*Ber.*, 3, 549); and finally, on adding water, the crystalline hydrazotoluene (m. p. 126°) already prepared by Werigo, is precipitated. The compound melting at 75°, and that melting at 70°, both have the composition $C_{14}H_{14}N_2O$, and determinations of their molecular weight by Raoult's method show that they are isomeric. They are named by the authors β-azoxytoluene and α-azoxytoluene respectively.

β-Azoxytoluene can also be obtained by oxidising parazotoluene with a small quantity of fuming nitric acid in glacial acetic acid solution. It crystallises in orange-yellow needles or prisms.

α-Azoxytoluene crystallises in pale yellow needles or plates, and is more readily soluble than the β-compound.

Azoxytoluenesulphonic acid is obtained when α-azoxytoluene is gradually added to a mixture of sulphuric acid and sulphuric anhydride, and the mixture heated at 80—90°. It is a brownish-red, amorphous mass, with a metallic lustre. The *potassium* salt and the *sodium* salt crystallise in golden plates. The *barium* salt, *lead* salt, and *silver* salt are sparingly soluble.

β-Azoxytoluene yields a disulphonic acid under the same conditions; the *potassium* salt of this acid crystallises in needles, the other salts are very readily soluble, and are not easily obtained in crystals.

α- and β-azoxytoluene appear to yield the same nitro-compound (m. p. 194—196°) when treated with fuming nitric acid, but acid of sp. gr. 1·41—1·45 reacts differently with these two substances.

When treated with bromine, the two azoxytoluenes yield several products, two of which seem to be identical. F. S. K.

Derivatives of Phenylhydrazine. By L. Marckwald (*Chem. Centr.*, 1888, 1410).—A mixture of ethylene bromide and phenylhydrazine in molecular proportion, when heated with an equal volume of alcohol in a reflux apparatus, yields, in addition to benzene, aniline hydrobromide and ammonium bromide, a base, $C_{16}H_{20}N_4$, melting at 178°; as this, when reduced by zinc-dust and acetic acid, gives a basic mixture containing aniline, the author infers that the constitution of the base is $(C_2H_4)_2(N_2HPh)_2$. Trimethylene bromide and phenylhydrazine, when submitted to similar treatment, give a substance of the formula $C_9H_{12}N_2$, melting at 52—53°. By heating it with trimethylene bromide in an oil-bath, a compound, $(PhN_2)_2(C_3H_6)_3$, melting at 224—226°, is formed.

Benzenyldiphenylazidine, $C_{19}H_{16}N_4$, prepared from benzotrichloride and phenylhydrazine, melts at 178—180°; it dissolves in alcoholic hydrogen chloride, and on evaporating the solution the hydrochloride is obtained as a colourless oil. When heated with carbon bisulphide at 100°, a compound melting at 136° is formed; by heating in hydrogen sulphide at 160—166° ammonia is liberated and a compound, $C_{38}H_{33}NS$, is obtained, melting at 62°. From the analysis of the platinochloride, it would seem to be bibasic. Plumbic oxide desulphurises it, and the product melts at 96°.

Phenylhydrazine and sulphocarbanilide, when boiled with plumbic oxide until completely desulphurised, yield *anildiphenylguanidine*, melting at 138—139°. This base dissolves in alcohol and becomes coloured superficially red, owing to oxidation. A bluish-black dye is found in the alcoholic mother-liquor, which is also formed from phenylhydrazine, diphenylsemicarbazide, and plumbic oxide, and has the formula PhNC·N·NPh·NH·NHPh. J. W. L.

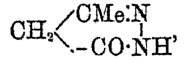
Condensation-products of Hydrazine with Aldehydes. By T. Curtius and R. Jay (*J. pr. Chem.*, **39**, 43—58).—*Benzalazine*, $N_2(CHPh)_2$, prepared by the action of benzaldehyde on crude hydrazine sulphate (see p. 340), crystallises from hot alcohol in long, lustrous, bright yellow, anisotropic prisms which melt at 93°, are insoluble in water and soluble in other solvents. It is decomposed by heat into nitrogen and stilbene, a secondary product of the formula $N_2(CHPh)_3$, melting at 78°, being also formed. The molecular formula of benzalazine has been established by Raoult's method. By reducing an alcoholic solution of benzalazine with sodium, benzylamine is formed; but if sodium amalgam is used, dibenzylhydrazine is formed.

Dibenzylhydrazine hydrochloride, $N_2H_2(CH_2Ph)_2,HCl$, crystallises from hot alcohol in small, lustrous, biaxial tables, melting at 140°, and very soluble in water.

Orthohydroxybenzalazine, $N_2(CH{\cdot}C_6H_4{\cdot}OH)_2$, is prepared by the action of salicylaldehyde on hydrazine salts; it crystallises in tables, insoluble in water and cold alcohol, and melts at 205°.

Orthonitrobenzalazine, $N_2(CH{\cdot}C_6H_4{\cdot}NO_2)_2$, prepared from orthonitrobenzaldehyde and hydrazine salts, crystallises in aggregates of bright-yellow needles melting at 181°.

Cinnamylidenazine, $[C_6H_5(CH)_3]_2N_2$, crystallises in long, yellow clinobasic tables melting at 162°. A condensation product of glyoxal and hydrazine has also been obtained.

Methylpyrazolone,  $CH_2<\begin{matrix}CMe{:}N\\ |\\ CO{\cdot}NH\end{matrix}$, is obtained when ethyl acetoacetate acts on hydrazine hydrate; it crystallises from water in vitreous prisms, and from alcohol in needles. It melts at 215°, sublimes unchanged in laminæ, tastes sweet, and dissolves in both acids and alkalis.

Symmetrical and asymmetrical azinsuccinic acids and their salts have been described before (Abstr., 1885, 885, 886). A. G. B.

Additive Compounds of Cyanic Acid. By W. Traube (*Chem. Centr.*, 1888, 1435).—*Benzyl allophanate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}COO{\cdot}C_7H_7$, prepared by passing cyanic acid into an ethereal solution of benzyl alcohol, melts at 183°. With benzyl alcohol, it forms *benzylurethane*, $NH_2{\cdot}COO{\cdot}C_7H_7$, melting at 83° and boiling at 235°; this forms substituted ethereal salts of allophanic acid with substituted salts of isocyanic acid. *Benzyl monophenylallophanate*, $NHPh{\cdot}CO{\cdot}NH{\cdot}COO{\cdot}C_7H_7$, melts at 158°. *Resorcinyl allophanate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}COO{\cdot}C_6H_4{\cdot}OH$, formed by the action of resorcinol on cyanic acid, melts at 120° with partial decomposition. A similar but more feeble reaction takes place with quinol. *Hydroxyphenylcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, is prepared from cyanic acid and orthoamidophenol. *Ethyl allophanyl-α-lactate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}COO{\cdot}CHMe{\cdot}COOEt$, melting at 170°, is prepared from cyanic acid and ethyl α-lactate, from which the free *allophanyl-α-lactic acid*, melting at 190°, is obtained by hydrolysis with hydrogen chloride. The silver and lead salts were prepared, also the amyl salt. *Ethyl allophanylglycollate* melts at 144°, and is not identical with the compound obtained by Saytzeff from chloracetic acid. The free acid melts at 192°. *Diethyl allophanyltartrate*, $C_{10}H_{16}O_8N_2$, melts at 188°; the free acid is a syrup, and is bibasic. J. W. L.

Oxidation of Benzene-derivatives with Potassium Permanganate. By W. A. NOYES (*Amer. Chem. J.*, **10**, 472—487; compare Abstr., 1886, 142; also Niementowski, Abstr., 1888, 873; and Niementowski and Rozanski, *ibid.*, 1088).—*β-Nitroparatoluic acid*,

$$NO_2{\cdot}C_6H_3Me{\cdot}COOH,$$

is formed when nitro-xylene (4 to 7 c.c.) is boiled for 3—4 hours with potassium ferricyanide (100 grams), potash (40 grams), and water (400 c.c.). The yield is not good, and the acid is best prepared as follows: nitroparatoluidine, obtained by Gattermann's method (*Ber.*, **18**, 1482), slightly modified, is converted into the cyanide, as described by Sandmeyer (*Ber.*, **18**, 1492), using a somewhat large amount of potassium cyanide to prevent the separation of cuprous cyanide at the end of the reaction. The cyanide crystallises in slender needles, melts at 100°, and is moderately soluble in alcohol, readily in ether. The cyanide is heated with strong hydrochloric acid (15 parts) at 150—160°, and the acid which separates is purified by dissolving in dilute ammonia, precipitating with hydrochloric acid, and crystallising from hot water. It forms slender needles, melts at 164—165° (corr.), and dissolves readily in hot water, alcohol, and ether. The *copper salt* (with 1 mol. H_2O) forms bright green, microscopic crystals, almost insoluble in water. The *barium salt* (with 5 mols. H_2O) separates in hemispherical groups of crystals readily soluble in water; the *calcium salt* (with 2 mols. H_2O) separates as a network of needles, much less soluble than the barium salt.

β-Amidoparatoluic acid, $NH_2{\cdot}C_6H_3Me{\cdot}COOH$, prepared by reducing the nitro-acid with tin and hydrochloric acid, crystallises in fine plates, usually brownish, melts at 177—178° (corr.) with decomposition, dissolves sparingly in water, readily in alcohol. The aqueous solution shows a bluish-violet fluorescence, which disappears on adding strong acid, and reappears on adding ammonia. The *barium salt* (with 4 mols. H_2O) crystallises in brown leaflets, very sparingly soluble in water; the *calcium salt* (with 2 mols. H_2O) separates in slightly brown scales; the *copper salt* is a light green, amorphous substance, almost insoluble in water. When the acid is dissolved in dilute sulphuric acid and treated with potassium nitrite, hydroxyparatoluic acid, [Me : OH : COOH = 4 : 2 : 1], is formed.

α-Nitroparatoluic acid was prepared from nitroparatoluidine in a manner similar to the β-acid. The *copper salt*, $(NO_2{\cdot}C_6H_3Me{\cdot}COO)_2Cu + 4H_2O$, crystallises in bright blue needles; *copper salts* of the formulæ $(C_7H_6NO_2{\cdot}COO)_4Cu_3(OH)_2 + H_2O$ and $(C_7H_6NO_2{\cdot}COO)_5Cu_3{\cdot}OH + H_2O$, were also obtained.

In the preparation of nitroparatoluic acid by oxidising nitroparaxylene with potassium ferricyanide, two more substances were obtained. The one melted at 266—268°, and was evidently nitroterephthalic acid (m. p. = 270°), the other separated in well-formed plates, having the same composition as nitroterephthalic acid, with the addition of 2 mols. H_2O. Various attempts were made to obtain these plates in other ways, but with negative results. It is therefore probable that the water (which the substance loses on heating) is not water of crystallisation but of constitution, and that the substance has the formula $NO_2{\cdot}C_6H_3[C(OH)_3]_2$.

β-Nitroisophthalic acid, [COOH : COOH : NO_2 = 1 : 3 : 4], prepared by oxidising nitrometaxylene, melts at 257—259°; it seems to be identical with Beyer's acid, obtained by nitrating isophthalic acid (*J. pr. Chem.* [2], **22**, 352). The *barium salt* (with 1½ mol. H_2O) crystallises in slightly yellow needles. N. H. M.

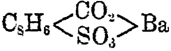
γ- and δ-Isatropic Acids. By C. Liebermann and, in part, W. Drory and O. Bergami (*Ber.*, **22**, 124—130; compare Abstr., 1888, 1211).—When γ-isatropic acid is distilled, it is converted into cinnamic acid and a small quantity of a substance insoluble in alkali, probably dicinnamyl. Calcium cinnamate crystallises with 3 mols. H_2O, and does not give up 1 mol. H_2O at the ordinary temperature (compare Kopp, *Compt. rend.*, **53**, 634); the anhydrous salt dissolves in 430 parts of water at 19° (compare Kraut, *Annalen*, **147**, 112).

δ-Isatropic acid also yields cinnamic acid when distilled; but a larger amount of the insoluble product seems to be formed.

γ-Isatropic anhydride, $(C_9H_7O)_2O$, is prepared by heating the acid (3 parts) with acetic anhydride (10 parts) and sodium acetate (4 parts) on a water-bath. On adding light petroleum to the benzene solution, it crystallises in white needles melting at 191°.

ε-Isatropic acid, $C_9H_8O_2$, is formed when the anhydride is dissolved in alkali and precipitated with hydrochloric acid. It crystallises from very dilute alcohol in needles melting at 228° and closely resembles the γ-acid, being readily soluble in ether and very sparingly soluble in hot water. The *barium salt* is very readily soluble. The acid is converted into cinnamic acid when distilled. The acid is also obtained by heating the anhydride of the γ-acid with hydrochloric acid at 160°. The *methyl salt* crystallises in lustrous needles melting at 126°, and is rather soluble in cold methyl alcohol and glacial acetic acid. The acid yields an anhydride identical with that obtained from the γ-acid.

δ-Isatropic anhydride, $(C_9H_7O)_2O$, is purified by dissolving the dry substance in benzene, carefully precipitating the resinous impurity with light petroleum, and letting the filtrate evaporate spontaneously. It forms rhombic crystals, melts at 116°, and is readily soluble in the usual solvents except water. When dissolved in alkali and precipitated with acid, the δ-acid is again formed.

When γ-isatropic acid is heated with sulphuric acid (8 to 10 parts) for three hours at 80°, two isomeric sulphonic acids are formed; on diluting with water (5 parts) and evaporating, the one (*a*) crystallises in slender needles, whilst the other (*b*) remains dissolved. The acids are readily separated by means of the barium salts. *Barium sulpho-γ-isatropate* (*a*),  $C_8H_6<\substack{CO_2\\SO_3}>Ba + 2H_2O$, forms a crystalline powder, insoluble in alcohol, sparingly soluble in hot water, very readily in cold water. When the sulphonic acid is heated at 220° with fuming hydrochloric acid, it is converted, with partial decomposition, into an isomeride which seems to be identical with the acid (*b*). *Barium sulpho-γ-isatropate* (*b*) with 2 mols. H_2O is readily soluble in cold and in hot water.

Barium sulpho-δ-isatropate, $C_9H_6SO_5Ba + 2H_2O$, was also prepared.

N. H. M.

Paranitrophenylbutinecarboxylic Acid. By A. EINHORN and C. GEHRENBECK (*Ber.*, **22**, 45—47).—*Paranitrophenylbutinecarboxylic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COOH$, obtained from paranitrocinnamaldehyde by Perkin's reaction, crystallises from dilute alcohol in yellowish needles melting at 271°. It combines with bromine with development of heat, forming the *tetrabromide*, $NO_2{\cdot}C_6H_4{\cdot}[CHBr]_4{\cdot}COOH$, which crystallises from alcohol in plates melting at 254° with decomposition.

Paranitrophenylbutinedicarboxylic acid,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}C(COOH)_2,$$

is formed by the condensation of paranitrocinnamaldehyde with malonic acid in glacial acetic acid solution. It crystallises in yellow needles melting at 208°.

Paranitrophenyldibromethylbromacrylic acid,

$$NO_2{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CBr{:}CH{\cdot}COOH,$$

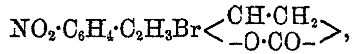
is formed, with evolution of hydrogen bromide and carbonic anhydride, when the preceding compound is treated with excess bromine; it is also obtained, in the form of the *sodium* salt, when th tetrabromide described above is dissolved in sodium carbonate. crystallises from alcohol in plates and melts at 205—206°. Wh the sodium salt is warmed with alkaline carbonates, it loses 1 mol. H and is converted into a compound, probably *paranitrophenyldibrom butinecarboxylic* acid, $NO_2{\cdot}C_6H_4{\cdot}C_2HBr{\cdot}CBr{:}CH{\cdot}COOH$, which crystallises from glacial acetic acid in light yellow plates melting 242—244°.

Paran[illegible]yldihydrodibromobutinecarboxylic acid,

$$NO_2{\cdot}C_6H_4{\cdot}C_2BrH_3{\cdot}CHBr{\cdot}CH_2{\cdot}COOH,$$

is produced, with evolution of carbonic anhydride, when paranitrophenylbutinedicarboxylic acid is treated with hydrobromic acid; melts at 146—147°.

The lactone of *paranitrophenylbromethyllactic acid,*



$$NO_2\cdot C_6H_4\cdot C_2H_3Br<\begin{matrix}CH\cdot CH_2\\ -O\cdot CO-\end{matrix}>,$$

is obtained when the preceding compound is neutralised with sodium carbonate and the solution kept for some time. It crystallises in colourless plates melting at 146°. When dissolved in a mixture of alcohol and ethyl acetate and treated with excess of sodium carbonate in the cold, it is converted into the lactone of *paranitrophenylvinylhydroxypropionic acid*, $NO_2\cdot C_6H_4\cdot CH{:}CH<\begin{matrix}CH\cdot CH_2\\ -O\cdot CO-\end{matrix}>$, melting at 110—111° This lactone can also be obtained by dissolving paranitrophenyldihydrodibromobutinecarboxylic acid in excess of sodium carbonate.

F. S. K.

Hydrazinesulphonic Acids and Triazo-compounds. By H. LIMPRICHT (*Ber.*, **21**, 3409—3423).—*Metahydrazinebenzenesulphonic* acid is prepared by gradually adding metadiazobenzenesulphonic acid to a well-cooled hydrochloric acid solution of stannous chloride, precipitating the tin, and concentrating the filtered solution. It crystallises in colourless plates or needles with 2 mols. H_2O, loses its water at 110°, and is not decomposed when heated at 200°. It is readily soluble in hot, sparingly in cold water, and almost insoluble in alcohol and ether; it is decomposed when warmed with ferric chloride, and it reduces Fehling's solution and solutions of silver under the same conditions. The compound $SO_3Na\cdot C_6H_4\cdot N_2H\cdot CHPh + 2H_2O$ is formed when the sodium salt is warmed with benzaldehyde in alcoholic solution. It crystallises in plates, loses its water at 110°, and is readily soluble in hot water, but sparingly in alcohol and ether. It is not decomposed at 100°, but by the action of acids it is reconverted into benzaldehyde and the acid.

Metatriazobenzenesulphonic acid, $N_3\cdot C_6H_4\cdot SO_3H$, is produced when nitrous acid is passed for a long time into alcohol containing the hydrazine-compound in suspension. It can also be prepared by mixing equivalent quantities of metadiazobenzenesulphonic acid and metahydrazinebezenesulphonic acid in presence of a small quantity of water. It crystallises in colourless, deliquescent needles, is decomposed when warmed with alkalis or when heated with hydrochloric acid, and yields metamidobenzenesulphonic when reduced with zinc and acetic acid. The *barium* salt, $(C_6H_4N_3SO_3)_2Ba$, crystallises in slender, colourless needles and explodes when heated at 130°.

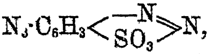
Metahydrazinebenzenedisulphonic acid, $N_2H_3\cdot C_6H_3\cdot (SO_3H)_2$, is obtained in small quantities when metahydrazinebenzenesulphonic acid is treated with chlorosulphonic acid; it is best prepared by treating metamidobenzenesulphonic acid with chlorosulphonic acid and reducing the barium salt of the diazodisulphonic acid, which is obtained on diazotising the product, with well-cooled stannous chloride and hydrochloric acid. It crystallises in slender, colourless, deliquescent needles, is readily soluble in alcohol and is decomposed when gently heated. It gives the hydrazine reaction with ferric chloride and Fehling's solution. The *barium* salt, $C_6H_6N_2S_2O_6Ba$, separates in reddish, nodular crystals when alcohol is added to the concentrated aqueous solution. The hydrogen barium sulphonate,

$$(C_6H_6N_2S_2O_6)_2BaH_2,$$

crystallises in thick needles and is rather sparingly soluble in water.

Parahydrazinebenzenedisulphonic acid, prepared by treating paramidobenzenedisulphonic acid as described above, crystallises in plates, decomposes at 120°, and is readily soluble in water and alcohol. The *barium* salt, $N_2H_3\cdot C_6H_3(SO_3)_2Ba$, is a yellow, crystalline, unstable compound; the *hydrogen barium sulphonate* crystallises from water in colourless, rhombic plates.

Potassium triazonitrobenzenesulphonate, $N_3\cdot C_6H_3(NO_2)\cdot SO_3K$, prepared by gradually adding hydrazinenitrobenzenesulphonic acid to a well-cooled, concentrated solution of potassium nitrite, crystallises in light brown plates, is very unstable, explodes when heated to 130°, and is readily soluble in hot water. It dissolves in excess of potash with a red coloration, but when boiled with potash or when treated with stannous chloride or ammonium sulphide in the cold, it is decomposed with evolution of nitrogen. When reduced with zinc-dust and acetic acid, it is converted into a very unstable substance, which is decomposed by cold ferric chloride and reduces Fehling's solution. It is partially decomposed, with evolution of nitrogen, when boiled for a long time with hydrochloric acid; and when heated for a long time with moderately concentrated sulphuric acid it is converted into nitranilinesulphonic acid.

Diazotriazobenzenesulphonic acid,  $N_3\cdot C_6H_3\left\langle\begin{array}{c}-N\\ SO_3\end{array}\right\rangle N$, is obtained when hydrazineamidobenzenesulphonic acid is suspended in alcohol and treated with nitrous acid. It is an orange-red, crystalline, very explosive substance, and quickly turns blue on exposure to the air. It is decomposed with evolution of nitrogen when boiled with water, but it does not reduce Fehling's solution. When treated with stannous chloride in the cold, it is converted into a very unstable and readily soluble, crystalline hydrazine-derivative.

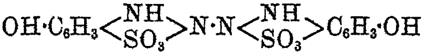
Paratriazorthotoluenesulphonic acid, [Me : SO_3H : N_3 = 1 : 2 : 4], is prepared by gradually adding the finely divided hydrazine acid to a very dilute solution of the corresponding diazo-derivative and keeping the mixture for 24 hours. It crystallises in colourless, deliquescent needles. The *barium* salt crystallises with 3 mols. H_2O in colourless needles. The corresponding *ortho*-acid is prepared in like manner, but the mixture of the diazo- and hydrazine-compounds must be kept for eight days; it resembles the preceding compound.

Diazodibromobenzenesulphonic acid separates in yellow crystals when a well-cooled solution of sodium dibromamidobenzenesulphonate is treated with sodium nitrite and hydrochloric acid. The yield is almost theoretical. It is very sparingly soluble in cold water, is decomposed by boiling water, and explodes violently when heated.

Hydrazinedibromobenzenesulphonic acid is formed when the diazo-compound is dissolved in a well-cooled hydrochloric acid solution of stannous chloride. It is sparingly soluble in warm water, and gives the hydrazine reaction with ferric chloride, Fehling's solution, and silver nitrate.

Triazodibromobenzenesulphonic acid, $N_3\cdot C_6H_2Br_2\cdot SO_3H$, is obtained together with metamidobenzenesulphonic acid, dibromamidobenzenesulphonic acid, and triazobenzenesulphonic acid, when the dibromhydrazine acid is treated with metadiazobenzenesulphonic acid or when diazodibromobenzenesulphonic acid is treated with metahydrazinebenzenesulphonic acid. It crystallises in small needles. The *barium* salt, $(N_3\cdot C_6H_2Br_2\cdot SO_3)_2Ba$, crystallises in pale red plates, is sparingly soluble in cold water, and explodes when heated

Hydrazobenzenedisulphonic acid is best prepared by warming metanitrobenzenesulphonic acid with zinc-dust and soda until the yellow colour, due to the formation of the azo-compound, has disappeared. The solution is quickly filtered, saturated with hydrogen chloride, and, after keeping for 24 hours, the precipitate is collected, dissolved in soda, and reprecipitated from the filtered solution by hydrochloric acid. The diazo-compound,

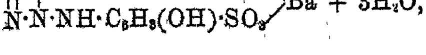


$$OH\cdot C_6H_3<\begin{smallmatrix}NH\\ SO_3\end{smallmatrix}>N\cdot N<\begin{smallmatrix}NH\\ SO_3\end{smallmatrix}>C_6H_3\cdot OH,$$

is most easily prepared by mixing a concentrated solution of sodium hydrazobenzenedisulphonate with the calculated quantity of sodium nitrite, and gradually adding hydrochloric acid to a well-cooled solution until the brown colour disappears. It yields a yellow, crystalline compound when heated with alcohol under pressure, and the smell of aldehyde is distinctly perceptible. (Compare Balentine, Abstr., 1880, 809.) The corresponding hydrazine-derivative is readily obtained by gradually adding the diazo-compound to a well-cooled hydrochloric acid solution of stannous chloride; the product is dissolved in hot soda, the filtered solution precipitated with hydrochloric acid, and the hydrazine boiled with water to remove sodium chloride. It is a yellow, crystalline powder, insoluble in most of the usual solvents, and explodes when heated. When mixed with cold hydrobromic acid, it yields the hydrobromide of the diazo-compound, which is converted into the diazo-derivative when treated with water. The *barium* salt, $NH_2\cdot N[NH\cdot C_6H_3(OH)\cdot SO_3]_2Ba,2H_2O$, crystallises in yellowish needles and is readily soluble in water.

Equivalent quantities of hydrazinebenzenedisulphonic acid and the diazo-compound were mixed together in presence of a large quantity of water; evolution of gas commenced and the solution became deep red. As, after several days, some of the hydrazine-compound was still undecomposed, more diazo-acid was added, whereupon *triazobenzenedisulphonic* acid separated after a short time. This acid is also formed, together with hydrazobenzenedisulphonic acid, metamidobenzenesulphonic acid, and triazobenzenesulphonic acid, when metahydrazinebenzenesulphonic acid is treated with the calculated quantity of diazohydrazophenoldisulphonic acid in ice-cold aqueous solution.

Barium triazobenzenedisulphonate,



$$\left.\begin{matrix}N\cdot N\cdot NH\cdot C_6H_3(OH)\cdot SO_3\\ \|\ \ \|\\ N\cdot N\cdot NH\cdot C_6H_3(OH)\cdot SO_3\end{matrix}\right>Ba + 3H_2O,$$

crystallises in yellowish plates, explodes when heated, and decomposes slowly at the ordinary temperature. F. S. K.

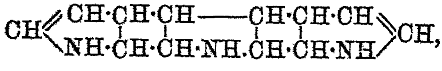
Aromatic Lead Compounds. By A. POLIS (*Ber.*, **21**, 3424—3428; compare Abstr., 1887, 572).—Lead tetratolyl is converted into chlorotoluene and lead chloride when heated at 200° with hydrochloric acid, and is decomposed when treated with cold, concentrated nitric acid.

Lead ditolyl chloride, $Pb(C_7H_7)_2Cl_2$, prepared by passing a stream of dry chlorine over a carbon bisulphide solution of lead tetratolyl, is a colourless powder, sparingly soluble in chloroform, carbon bisulphide, and benzene, and insoluble in ether and alcohol. It is decomposed when heated, and is converted into the corresponding nitrate when treated with alcoholic silver nitrate. The *bromide*, $Pb(C_7H_7)_2Br_2$, is prepared by gradually mixing lead tetratolyl and bromine in carbon bisulphide solution; it resembles the chloride in all respects. The *iodide*, $Pb(C_7H_7)_2I_2$, prepared in like manner, is a yellow powder, and is more readily soluble in chloroform and carbon bisulphide than the chloride or bromide.

The *nitrate*, $Pb(C_7H_7)_2(NO_3)_2 + 3H_2O$, is obtained by gradually adding finely divided lead tetratolyl to boiling nitric acid of sp. gr. 1·4, and finally concentrating the solution. It crystallises in very small, colourless needles, is sparingly soluble in alcohol and dilute nitric acid, and explodes when heated. The *salt* $OH{\cdot}Pb(C_7H_7)_2{\cdot}NO_3$ is formed when the nitrate is heated with water, or when a dilute nitric acid solution of this salt is treated with ammonia; it is a white, amorphous powder, and explodes slightly when heated.

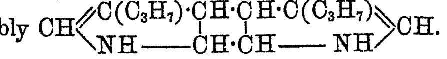
The *acetate*, $Pb(C_7H_7)_2(C_2H_3O_2)_2 + 2H_2O$, prepared by dissolving lead tetratolyl in boiling acetic acid, crystallises in needles, melts at 183·5°, and is moderately soluble in alcohol and dilute acetic acid. The *formate*, $Pb(C_7H_7)_2(CHO_2)_2$, crystallises in colourless needles, decomposes at 233°, and resembles the acetate in its behaviour towards solvents. The *chromate*, $Pb(C_7H_7)_2CrO_4$, is precipitated when a solution of the acetate is mixed with potassium bichromate; it is a yellow powder, and is insoluble in the ordinary solvents. The *sulphide*, $Pb(C_7H_7)_2S$, prepared by treating a solution of the acetate with hydrogen sulphide, is a yellow, crystalline compound which begins to decompose at 90° and melts at 98°. It is very readily soluble in benzene, carbon bisulphide, and chloroform, but sparingly in alcohol and ether, and decomposes on exposure to light. F. S. K.

Conversion of Pyrroline-derivatives into Indole-derivatives. By M. DENNSTEDT (*Ber.*, **21**, 3429—3440).—The compound obtained by passing dry hydrogen chloride into an ethereal solution of pyrroline (compare Dennstedt and Zimmermann, Abstr., 1888, 849) is *tripyrroline*, the constitution of which is probably



and the compound obtained in like manner from isopropylpyrroline
]

(*loc. cit.*) is diisopropyldipyrroline, the constitution of which is probably



$$\mathrm{CH}\begin{matrix}\diagup\mathrm{C(C_3H_7)\cdot CH\cdot CH\cdot C(C_3H_7)}\diagdown\\ \diagdown\mathrm{NH}\text{——}\mathrm{CH\cdot CH}\text{——}\mathrm{NH}\diagup\end{matrix}\mathrm{CH.}$$

3 . 3′ *Diisopropylindole*, $C_{14}H_{19}N$, is obtained by mixing an aqueous solution of diisopropyldipyrroline hydrochloride with dilute sulphuric acid, and, after keeping the mixture for some time at the ordinary temperature, distilling the product with steam. A dark oil collects in the receiver at the commencement of the process, but the longer the distilling is continued the purer is the product obtained, so that finally the oily distillate solidifies. As the base is only very slightly volatile with steam but readily volatile with alcohol vapour, alcohol is added after some time and the distillation continued. The yield of the crude product is about 50 per cent. of the theoretical quantity. The crystals, after separation from oily impurities by filtration, are dissolved in a small quantity of alcohol and boiled with animal charcoal; water is then carefully added to the filtered solution until a turbidity is produced, crystallisation being promoted by rubbing. This process is repeated until a colourless product is obtained, and the indole is then finally recrystallised from dilute alcohol.

Diisopropylindole can also be prepared by dissolving isopropylpyrroline in dilute sulphuric acid, keeping the mixture for 24 hours, and purifying the product in the manner described above. It crystallises in colourless needles, melts at 65°, and boils at 295—300° with slight decomposition. It gives the pinewood reaction, is very readily soluble in alcohol, acetone, ether, glacial acetic acid, chloroform, &c., and dissolves in concentrated hydrochloric acid, but is reprecipitated unchanged on adding water. The *picrate* separates in red needles when an alcoholic solution of equivalent quantities of diisopropylindole and picric acid is gradually evaporated; it melts at 115°, dissolves in alcohol with a yellow coloration, and is insoluble in cold water, but dissolves on boiling and is decomposed. When diisopropylindole is melted with 20 to 30 times its weight of anhydrous potash, a small quantity of a colourless, crystalline acid is obtained; if this acid is gradually heated, carbonic anhydride is evolved and indole is probably formed. When the base is treated with the calculated quantities of sodium nitrite in glacial acetic acid solution, the mixture darkens in colour, and, on carefully adding water or acetic acid, a yellow, crystalline precipitate separates; this precipitate does not show the nitroso-reaction.

Benzylidinediisopropylindole, $C_{35}H_{42}N_2$, is formed when diisopropylindole (2 parts) is heated with benzaldehyde (1 part) and a small quantity of zinc chloride. It is a yellowish, crystalline compound, melts at 162—165° with decomposition, and is readily soluble in most of the ordinary solvents, but is precipitated from its alcoholic solution on adding water.

Diisopropylindole and metanitrobenzaldehyde yield, under the same conditions, a condensation product melting at 185°, and the condensation product with phthalic anhydride is a dark-red, crystalline substance, which is decomposed when boiled with water.

An *acetyl*-derivative, $C_{11}H_{21}NO$, is obtained when the indole is heated at 180—190° with acetic anhydride and sodium acetate; it crystallises in yellowish needles melting at 185—186°, is insoluble in water, and is hydrolysed when boiled for a long time with hydrochloric acid, but is not decomposed by boiling potash. Silver nitrate, in presence of ammonia, produces a white, crystalline precipitate in an alcoholic solution of the acetyl-derivative.

Diisopropylmethyldihydroquinoline is formed when diisopropylindole (1 part) is heated at 120° for 15 hours with methyl alcohol (1 part) and methyl iodide ($2\frac{1}{2}$ parts). The mixture is distilled with steam until no more oil passes, then made alkaline and the distillation continued. The yellowish oil which collects in the receiver is dissolved in hydrochloric acid, the solution is shaken with ether, and, after acidifying, the base is extracted with ether, dried, and distilled. It is a yellowish oil, boils at 298—300° with partial decomposition, and gradually turns rose-coloured on exposure to the air. The *hydrochloride* is a colourless, vitreous mass. The *platinochloride*, $(C_{16}H_{23}N)_2,H_2PtCl_6$, is a light-yellow substance, melts at 177° with decomposition, and is insoluble in water. The *mercurochloride* is a white, amorphous, and the *picrate* is a yellow, crystalline compound.

When dimethyldipyrroline hydrochloride, prepared by passing hydrogen chloride into an ethereal solution of α-methylpyrroline boiling at 147—148°, is treated with dilute sulphuric acid as described above, a yellowish oil, boiling at about 275°, is obtained. This base is soluble in concentrated hydrochloric acid, but is reprecipitated on adding water. The *picrate*, $C_{10}H_{11}N,C_6H_3N_3O_7$, separates in dark-red crystals when a benzene solution of the base is mixed with a benzene solution of picric acid and evaporated; it softens at 150° and melts at 155—156° with decomposition. The base obtained in like manner from β-methylpyrroline, boiling at 142—143°, has a strong scatole-like smell, and boils at about 270°; it dissolves in concentrated hydrochloric acid, but is reprecipitated on adding water. The *picrate*, $C_{10}H_{11}N,C_6H_3N_3O_7$, crystallises in red needles and melts at 149°. F. S. K.

Derivatives of Paradiphenol. By H. Schütz (*Ber.*, **21**, 3530—3534).—Metadinitroparadiphenol (Kunze, this vol., p. 262) melts at 280° (not 272°), is insoluble in alcohol, sparingly soluble in glacial acetic acid. The *diacetyl-compound* forms straw-coloured needles melting at 215°; the *dibenzoyl-derivative* crystallises in colourless plates melting at 206°. Both compounds dissolve readily in hot glacial acetic acid.

Metadiamidoparadiphenol sulphate, $C_{12}H_6(NH_2)_2(OH)_2,H_2SO_4$, separates in needles; the *picrate* crystallises in groups of needles. The *diacetyl*-derivative forms white needles melting at 210°. When the base is heated with acetic chloride at 150°, diethenyldiamidodiphenyl, melting at 195°, is formed.

Tetranitrodiphenol melts at 225° (not 220°). The *sodium salt*, $C_{12}H_4(NO_2)_4(ONa)_2$, crystallises in red, lustrous needles, soluble in hot water; on cooling, the *salt*, $C_{10}H_4(NO_2)_4(ONa)\cdot OH$, separates in brownish-red needles. The *diacetyl-compound*, $C_{12}H_4(NO_2)_4(OAc)_2$, forms yellow, sparingly soluble needles, melting at 236°.

Tetramidodiphenol crystallises in plates of a silvery lustre and is very unstable. The *sulphate* and *picrate* crystallise in white needles and reddish-yellow needles respectively. The *hexacetyl-derivative*, $C_{12}H_4(NHAc)_4(OAc)_2$, is a white, crystalline powder; when heated with aqueous soda, the *tetracetyl-compound*, $C_{12}H_4(NHAc)_4(OH)_2$, is obtained. This forms lustrous needles melting at 280°. Acetic chloride acts on tetramidodiphenol with formation of the compound $C_{16}H_{14}N_4O_2$, which, on prolonged boiling with hydrochloric acid, yields tetramidodiphenol hydrochloride. N. H. M.

Isomerism of the Benzildioximes. By K. Auwers and V. Meyer (*Ber.*, **21**, 3510—3529).—*α-Benzildioxime dimethyl ether*, $C_{16}H_{16}N_2O_2$, is obtained, together with a non-ethereal isomeride, by treating the α-dioxime (10 grams) with methyl iodide (50 grams) and diluting with methyl alcohol; the whole is gently boiled for some hours in a reflux apparatus, during which time a solution of sodium (7·5 grams) in methyl alcohol is gradually added (compare Japp and Klingemann, *Annalen*, **247**, 201). The method employed for the separation of the products is described in detail. The dimethyl ether crystallises in well-formed, lustrous, triclinic prisms, melts at 109—110°, dissolves very readily in benzene, chloroform, &c., more sparingly in alcohol and ether, and is insoluble in cold water. It unites with hydrogen chloride, yielding the compound $C_{16}H_{16}N_2O_2{\cdot}HCl$, which forms short, lustrous prisms melting at 157—158° with evolution of gas; it is decomposed by cold water.

The *isomeride*, $C_{16}H_{16}N_2O_2$, crystallises from alcohol in small, lustrous prisms, melts at 165—166°, dissolves readily in benzene, chloroform, and carbon bisulphide, sparingly in alcohol, ether, and glacial acetic acid, and is insoluble in cold water.

Besides the two compounds just described, a base, $C_{16}H_{14}N_2$, and benzil are formed in the reaction; both these substances are also formed in a similar manner from β-benzildioxime.

β-Benzildioximedimethyl ether, $C_{16}H_{16}N_2O_2$, prepared in a manner similar to the α-compound, crystallises in rosettes of slender, white needles, melts at 88—89°, dissolves very readily in benzene, chloroform, and carbon bisulphide, readily in alcohol and ether, and is insoluble in cold water. The *hydrochloride*, $C_{16}H_{16}N_2O_2,HCl$, resembles the corresponding α-derivative very strongly, but melts at about 130°.

The non-ethereal *isomeride* of the β-dioxime forms flat, lustrous needles, melts at 72—73°, and is very readily soluble in ether, benzene, and chloroform, readily soluble in glacial acetic acid, less in alcohol.

The *base*, $C_{16}H_{14}N_2$, which is formed from both dioximes, crystallises from dilute alcohol in long, slender needles of a silky lustre, melts at 158—159°, is insoluble in water, readily soluble in alcohol, benzene, and carbon bisulphide, very readily in chloroform. The *nitrate* forms sparingly soluble, flat needles; the *platinochloride*, $(C_{16}H_{14}N_2)_2,H_2PtCl_6$, crystallises in lustrous, gold-coloured plates. The base is isomeric with Japp and Wynne's methyldiphenylglyoxaline (Trans., 1886, 462) and with Mason's diphenyldihydropyrazine (Abstr., 1887, 493).

All four isomerides ($C_{16}H_{16}N_2O_2$) yield dibenzyl when reduced with phosphorus and hydriodic acid.

When the α-dioxime dimethyl ether is heated with alcohol at

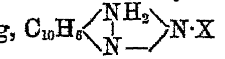
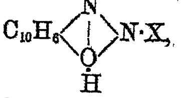
170—180° it is more or less decomposed, whilst the non-ethereal isomeride remains unchanged even at 240—250°.

When the α- and β-dioxime ethers are heated with strong hydrochloric acid for 10 hours at 100°, they are decomposed into benzil and methylhydroxylamine; the latter is further decomposed. Under similar conditions, the non-ethereal compound, $C_{16}H_{16}N_2O_2$, from the α-dioxime is converted almost quantitatively into that of the β-dioxime, whilst this compound is not acted on at all by hydrochloric acid at 100; at 170° it is converted into benzoic acid and ammonia. No benzil is formed in either case.

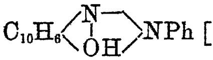
Both α- and β-benzildioxime, when reduced with zinc-dust and aqueous soda, yield tetraphenylaldine, benzil, a non-nitrogenous substance melting at 54°, probably dibenzyl, and several other compounds which were not examined.

Attempts were made to obtain an isomeride of dimethylglyoxine, but without success, a result which supports the authors' views as to the isomerism of the benzildioximes. N. H. M.

β-Naphthol Sulphide. By S. ONUFROWICZ (*Ber.*, **21**, 3559—3563).—β-Naphthol sulphide, $S(C_{10}H_6\cdot OH)_2$, is prepared by heating β-naphthol (250 grams) and sulphur (55 grams) at 170—180° for some hours. The product is boiled with alcohol in a reflux apparatus, filtered hot, and the brown prisms which separate recrystallised from alcohol. It is colourless, melts at 215°, is insoluble in water, ether, and benzene, soluble in alcohol. The *diacetate*, $S(C_{10}H_6\cdot OAc)_2$, forms slender, white needles, melts at 154°, and is sparingly soluble in ether and cold alcohol, readily in hot benzene. The *dibenzoate*, $S(C_{10}H_6\cdot OBz)_2$, crystallises in long, white plates, melts at 208°, dissolves readily in hot benzene, sparingly in ether and alcohol. When β-naphthol sulphide is heated with copper at 230—240°, β-dinaphthol, melting at 212°, is formed. N. H. M.

Evidence of Quantivalence of Oxygen derived from the Study of the Azo-naphthol Compounds. By R. MELDOLA (*Phil. Mag.* [5], **26**, 403—413).—After reviewing the different formulæ proposed for the azo-β-naphthol and naphthylamine compounds, the author suggests a closed ring,  $C_{10}H_6\left<\begin{matrix}NH_2\\|\\N\end{matrix}\right>N\cdot X$ (X = an aromatic radicle), for the azo-β-naphthylamines, the ring being formed by the interaction of the azo- and amido-groups. Such a formula would explain the difficulty with which they form salts and diazo-compounds, the acid having first to break the nitrogen-ring. From this formula, the azimides are easily derived by the removal of hydrogen. From the analogy between the β-naphthylamine and β-naphthol-derivatives, a similar formula,  $C_{10}H_6\left<\begin{matrix}N\\|\\O\\H\end{matrix}\right>N\cdot X$, is obtained for the latter. The only objection to this view is that it requires that oxygen should be tetravalent. This, however, is in accordance with later researches, and with the position of oxygen in the periodic system. It is also required by Friedel's compound OMe_2HCl.

The benzene-azo-β-naphthol, formed by the action of diazobenzene salts on β-naphthol, can be represented by the formula



$$C_{10}H_6\left\langle\begin{matrix}N-\\ |\\ OH\end{matrix}\right\rangle NPh\ [N = \alpha;\ O = \beta],$$

whilst the nitrogen- and oxygen-atoms hold a reversed position in the compound produced by the action of phenylhydrazine on β-naphthaquinone: hence the insolubility in alkali is due to the fact that the H is non-hydroxylic, but is attached to an oxygen-atom forming part of a closed chain. The above constitution may be applied to all amidoazo- and oxyazo-compounds of the ortho-series. H. K. T.

Action of Sunlight on Organic Compounds. By H. Klinger (*Annalen*, **249**, 137—146).—The action of light on ethereal solutions of benzil and phenanthraquinone has been previously investigated by the author (Abstr., 1886, 885). When a mixture of phenanthraquinone and acetaldehyde, isovaleraldehyde, or benzaldehyde is exposed to sunlight in sealed tubes, combination takes place resulting in the formation of acetylphenanthraquinol, isovalerylphenanthraquinol, or monobenzoylphenanthraquinol respectively. Phenanthraquinone appears to behave in a similar way with furfuraldehyde, salicaldehyde, and grape-sugar. It is remarkable that exposure to blue light is much more favourable to these changes than the action of red rays.

Anthraquinone, naphthaquinone, benzil, and benzoquinone appear to yield ethers of quinhydrone when they are exposed to the light in contact with aldehydes. W. C. W.

Action of Halogens on Rufigallol. By C. S. S. Webster and L. G. Hunt (*Chem. News*, **59**, 40—41).—When chlorine acts on rufigallol in acetic acid solution, *dichlorhexahydroxyanthraquinone* is obtained in nodules of brilliant-red, microscopic prisms. A bromine-derivative, obtained in a similar manner at 80°, crystallises from absolute alcohol in light-red, microscopic needles. D. A. L.

Chrysene Hydrides. By C. Liebermann and L. Spiegel (*Ber.*, **22**, 135—137).—*Chrysene perhydride*, $C_{18}H_{30}$, is obtained together with the hydride, $C_{18}H_{28}$, when chrysene (1 part), phosphorus (1 part), and hydriodic acid (sp. gr. = 1·7, 5 parts) are heated for 16 hours at 250—260°. The product is diluted with water, filtered, washed, and dissolved in dilute alcohol. The perhydride separates in slender, white needles; it melts at 115°, boils at 353° (corr.), and dissolves very readily in hot alcohol; it dissolves in bromine unchanged, and is not affected by cold nitric acid (sp. gr. = 1·48). Chromic acid oxidises it when boiled, but without yielding chrysoquinone. When treated with sulphuric acid, only a small amount of sulphonic acid is formed. When distilled over zinc-dust, chrysene is formed in considerable amount. It does not give a compound with picric acid.

Chrysene heckaidecahydride, $C_{18}H_{28}$, which remains as an oil on evaporating the mother-liquor from the above compound, is purified by freezing and spreading on cooled porous plates, which absorb the liquid hydrocarbon. The solid hydrocarbon is then removed mechanically, whilst the liquid is extracted from the plates by means of ether. The substance is dried, and at the same time freed from traces of iodine and hydrogen iodide by digesting it with sodium at 200° for a long time. It is a colourless, slightly fluorescent, viscid oil, without odour, boiling at about 360°. In its chemical properties it resembles the perhydride.

N. H. M.

Chemical Composition of the Russian White Resin from Pinus silvestris. (Part I.) By V. SHKATELOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 477—485).—Owing to the discrepancies in the results obtained with the resin of *Pinus maritima*, *P. larix*, and *P. abies*, and the uncertain composition of pimaric, sylvic, pinic, and abietic acids, the author has investigated the crystalline acid from the Russian resin obtained from *Pinus silvestris*, growing in the Archangel and Wologda Governments. In order to remove the uncrystallisable substances, the resin, ground fine, was extracted with alcohol of 50—60 per cent. (Maly, *J. pr. Chem.*, **86**, 111), and the residue, which was much whiter than before, was now treated with boiling spirit; the filtered alcoholic solution, after remaining some time, becomes almost entirely converted into a crystalline mass. The crystals were washed with alcohol of 85 per cent. and again recrystallised. After thrice repeating this process, 30 per cent. of a perfectly white product was obtained; whereas on repeating the same process with a resin that had been exposed to the action of air for one year, only 20 per cent. was obtained. In order to prevent this from becoming yellow and oxidising in the air, the operations have to be carried on as quickly as possible; finally a compound, melting at 143°, was obtained. The acid, $C_{40}H_{58}O_5$, is insoluble in water, but easily soluble in alcohol, ether, acetic acid, and liquid hydrocarbons. After fusion, it solidifies to an amorphous, transparent mass, and when heated above 360°, a colourless, uncrystallisable distillate passes over. The rotatory power of the alcoholic solution was found, $[\alpha]_j = -73{\cdot}59°$. It decomposes alkaline carbonates with liberation of carbonic anhydride, and the original acid is reprecipitated from the solution on adding a mineral acid. By the action of hydrogen chloride on the alcoholic solution, the acid is converted into an isomeric acid of the same composition—but of different properties, as it melts at 159—160°, and the rotatory power is $[\alpha]_j = -92{\cdot}58°$. From the sodium salt of the original acid, other salts of the following composition were obtained: $C_{20}H_{29}AgO_3$; $(C_{20}H_{29}O_3)_2Ba + 2H_2O$; $(C_{20}H_{29}O_3)_2Ca$, and $(C_{20}H_{29}O_3)_2Cu$. The acid $C_{40}N_{58}O_5$ appears to be a partial anhydride of an acid which gives the above salts, and whose formation may be represented as follows:—$C_{40}H_{58}O_5 + H_2O = 2C_{20}H_{30}O_3$. The ethyl salt, $C_{20}H_{29}O_3Et$, was obtained as a heavy oil by acting on the silver salt with ethyl iodide. On distillation, it decomposes with elimination of water and the formation of another ethyl salt, according to the equation $C_{20}H_{29}O_3Et = C_{20}H_{27}O_2Et + H_2O$. This new compound is a heavy, yellow oil which yields a resin with potassium hydroxide. Finally the author shows that the resinification of the acid when exposed to the air consists in an oxidation accompanied by loss of water. The acid described above agrees in properties with Maly's abietic acid, but differs from it in composition. B. B.

Apiole. By G. Ciamician and P. Silber (*Ber.*, **22**, 119—121; compare Abstr., 1888, 1100).—Apiolic acid (2 grams), potash (6 grams), and absolute alcohol (10 grams) were heated at 180° for four to six hours, the product evaporated on a water-bath, dissolved in water, acidified, and extracted with ether. On distilling the brown syrup left after evaporating the ether, a liquid was obtained which had an odour of phenol, and soon solidified. By repeating the operation several times, the substance was obtained pure. The new compound, $C_6H_2(OH)_2(OMe)_2$, melts at 105—106°, boils at 298°, and is soluble in ether, alcohol, benzene, hot water, and in potash. The *potassium-derivative* forms slender, dark-brown, bronze-like needles. The compound gives with ferric chloride a violet-black colour which changes to brownish-black. The *acetyl-derivative* melts at 143°.

When isoapiole is heated with alcoholic potash, it yields the same phenol ether.

Apiolaldehyde is best obtained by oxidising isoapiole with alkaline permanganate solution, extracting with ether and treating the ethereal solution with sodium hydrogen sulphite. *Apionacrylic acid*, prepared by Perkin's method from apiolaldehyde, crystallises in needles melting at 196°. N. H. M.

Crystalline Compound from glabrous Strophantus. By Arnaud (*Compt. rend.*, **107**, 1162—1164; compare Abstr., 1888, 848 and 1310).—The seeds of the glabrous *Strophantus* of Gabon, which constitute Inée or Onaye, the arrow-poison of the Pahouins, was treated in practically the same way as *S. kombé* (*loc. cit.*). They yield 4·7 per cent. of transparent, rectangular lamellæ which become thick and opaque if they form slowly. The crystals become pasty when heated, and melt at about 185°; they contain 17—18 per cent. of water, which is all expelled above 120° but is not given off in air dried by sulphuric acid. They dissolve in 150 parts of water at 8°, and a 6·5 per cent. solution at 50° has a rotatory power $[\alpha]_D = -33° 8'$. When heated with dilute acids, this substance yields a sugar and a peculiar resin.

The properties of this compound agree with those of ouabaine from Acokantheria, and it is identical in composition, the substance dried at 100° having the formula $C_{30}H_{46}O_{12} + H_2O$. The original crystals contain 7 mols. H_2O, six of which are expelled below 100°, but the seventh is not driven off below 120°. C. H. B.

Ergosterin. By C. Tanret (*Compt. rend.*, **108**, 98—100).—Ergot of rye contains a crystallisable substance which has always been regarded as cholesterin. If the ergot is treated with several times its weight of alcohol, the alcoholic extract distilled, and the residue treated with ether, the ethereal solution on distillation leaves an oily residue containing crystals. These are drained and recrystallised, first from alcohol containing alkali and afterwards from pure alcohol. The yield is about 0·2 gram per kilo.

The crystals have the composition $C_{26}H_{40}O_2 + H_2O$, and lose their water when heated at 110° or if fused in a vacuum. They separate from alcohol in nacreous plates and from ether in slender needles, dissolve in alcohol and ether, and are especially soluble in chloroform. They melt at 154°, boil at 185° under a pressure of 20 mm., and are lævogyrate; $[\alpha]_D = -114°$ in a chloroform solution; sp. gr. of the fused substance 1·040.

This compound, *ergosterin*, oxidises when exposed to the air, with development of a colour and odour, the change taking place rapidly at 100°. It is not attacked by boiling concentrated solutions of the alkalis. It has an alcoholic function and yields an *acetate*, $C_{26}H_{39}O{\cdot}OAc$, which crystallises in anhydrous, nacreous plates, insoluble in water and almost insoluble in cold alcohol, but readily soluble in hot alcohol and ether, and melting at 169° with decomposition; rotatory power $[\alpha]_D = -80°$. The *formate* has similar properties and melts at 154°, rotatory power $[\alpha]_D = -93° 4'$; the *butyrate* is very soluble in ether, from which it is precipitated by alcohol, melts with decomposition at 95°, and has a rotatory power $[\alpha]_D = -57°$.

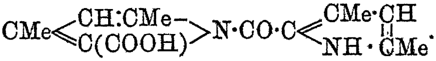
With nitric acid, hydrochloric acid and ferric chloride, ergosterin gives reactions very similar to those of cholesterin, but if the latter is treated with sulphuric acid, it turns brown and does not dissolve completely, and if the product is agitated with chloroform the latter acquires an orange-yellow colour which becomes red and then violet when exposed to the air. Ergosterin, on the other hand, is completely dissolved by sulphuric acid without discoloration, and chloroform remains almost colourless when agitated with the solution.

C. H. B.

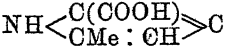
Embelic Acid. By C. J. H. WARDEN (*Pharm. J. Trans.* [3], **19**, 305).—From *Embelia ribes*, the author has isolated *embelic acid*, $C_9H_{14}O_2$, which he has obtained from its alcoholic solution in the form of crystals, insoluble in water, and melting at 140° to a deep-red liquid; they begin to decompose at 155°, with indications of partial sublimation. The alkali, lead, and silver salts were prepared. The ammonium salt was found effective as an anthelmintic for tænia; it has the advantage of being tasteless.

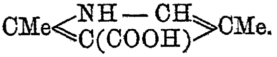
R. R.

Derivatives of Metadimethylpyrroline. By G. MAGNANINI (*Ber.*, **22**, 35—40).—The compound which is obtained by boiling tetramethylpyrocoll (dimethylpyrocoll) with alcoholic potash until the whole is dissolved (compare Magnanini, this vol., p. 57) is *tetramethylpyrroylpyrrolinecarboxylic acid*, $C_{14}H_{16}N_2O_3$. It is a monobasic acid, but the salts, especially the ammonium salt, are very unstable and are readily decomposed with formation of tetramethylpyrocoll when warmed in aqueous solution. The *barium* salt, $(C_{14}H_{15}N_2O_3)_2Ba$, crystallises in rhombic plates. The *methyl* salt, $C_{15}H_{18}N_2O_3$, melts at 163—163·5°, is readily soluble in chloroform and moderately soluble in ethyl acetate and benzene, but only sparingly in light petroleum, and insoluble in water. It is very unstable, and when heated above its melting point, when boiled with dilute alcohol, or when warmed with sodium carbonate solution, is converted into tetramethylpyrocoll. The acid is decomposed, with evolution of carbonic anhydride, when heated at 145°, and is converted into a crystalline compound, probably tetramethylpyrroylpyrroline, which is insoluble in alkalis. The molecular weight determined by Raoult's method is 287 as a mean of two experiments in benzene solution, but determinations in glacial acetic solution gave results varying from 174 to 239 as the concentration was increased from 0·5382 to 2·0860. Its constitution is



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH{:}CMe-}\\ \mathrm{C(COOH)}\end{matrix}>\mathrm{N\cdot CO\cdot C}<\begin{matrix}\mathrm{CMe\cdot CH}\\ \mathrm{NH\cdot CMe}\end{matrix}.$$

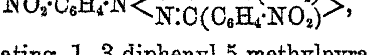
Dimethylpyrrolinecarboxylic acid, $C_7H_9NO_2$, is obtained when tetramethylpyrroylpyrrolinecarboxylic acid (1 part) is boiled with potassium hydrate (4 parts) and water (20 parts) until the formation of dimethylpyrroline commences. The product is precipitated with acetic acid, dried, dissolved in benzene, decolorised with animal charcoal, and precipitated from the concentrated solution with light petroleum. It melts at 137°, and is sparingly soluble in cold water, but dissolves in warm water with partial decomposition into carbonic anhydride and dimethylpyrroline. It is converted into tetramethylpyrocoll when boiled with acetic anhydride and then heated alone. A neutral solution of the ammonium salt gives precipitates with lead acetate, copper acetate, and ferric chloride. The constitution of this acid is probably  $\mathrm{NH}<\begin{matrix}\mathrm{C(COOH)}\\ \mathrm{CMe:CH}\end{matrix}>\mathrm{CMe}$, and that of the isomeric compound obtained by Knorr (Abstr., 1887, 275),



$$\mathrm{CMe}<\begin{matrix}\mathrm{NH-CH}\\ \mathrm{C(COOH)}\end{matrix}>\mathrm{CMe}.$$

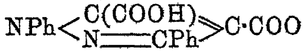
F. S. K.

Pyrazole and Pyrazoline. By L. Knorr and H. Laubmann (*Ber.*, **22**, 172—181).—*Trinitrodiphenylmethylpyrazole*,

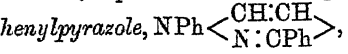


$$\mathrm{NO_2\cdot C_6H_4\cdot N}<\begin{matrix}\mathrm{CMe{=}C(NO_2)}\\ \mathrm{N{:}C(C_6H_4\cdot NO_2)}\end{matrix}>,$$

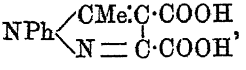
is obtained by heating 1.3-diphenyl-5-methylpyrazole (from ethyl benzoylacetate) with nitric acid (10 parts) and sulphuric acid (15 parts) on a water-bath until no more red fumes are given off. It melts at 176—178°, is insoluble in water and light petroleum, very sparingly soluble in ether and alcohol, readily in chloroform, benzene, and glacial acetic acid.

Diphenylpyrazoledicarboxylic acid,  $\mathrm{NPh}<\begin{matrix}\mathrm{C(COOH)}\\ \mathrm{N{=}CPh}\end{matrix}>\mathrm{C\cdot COOH}$, is formed by boiling potassium diphenylmethylpyrazolecarboxylate with 10 per cent. aqueous permanganate in a reflux apparatus for a long time; it is then freed from the excess of permanganate and from the manganese peroxide, and precipitated with dilute sulphuric acid. It crystallises from acetic acid in lustrous needles, having the composition $3C_{17}H_{12}N_2O_4 + H_2O$, melts at 217—218°, dissolves readily in alcohol and hot glacial acetic acid, sparingly in ether, chloroform, and water. The *hydrogen ammonium salt*, $C_{17}H_{15}N_3O_4$, crystallises in needles which melt at 270° with decomposition. The *barium salt*,

$C_{17}H_{10}N_2BaO_4 + H_2O$, crystallises in slender needles; the *calcium salt*, with 2 mols. H_2O, separates in microscopic needles.

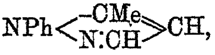
1.3-*Diphenylpyrazole*,  $NPh<\begin{matrix}CH{:}CH\\N{:}CPh\end{matrix}>$, obtained by distilling the dicarboxylic acid, is obtained as a thick, colourless, strongly refractive oil which becomes crystalline when kept a few days. It melts at 56° and boils at 337° under 736 mm. pressure. It is a feeble base. When reduced with sodium and alcohol, 1.3-*diphenylpyrazoline*, $C_{15}H_{14}N_2$, melting at 135—136°, is formed (compare Beyer and Claisen, Abstr., 1887, 743, and Claisen and Fischer, Abstr., 1888, 690).

1-*Phenyl*-5-*methylpyrazole*-3.4-*dicarboxylic acid*,

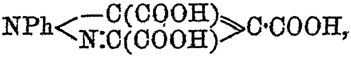


$$NPh\langle\begin{matrix}CMe{:}C{\cdot}COOH\\N = C{\cdot}COOH\end{matrix},$$

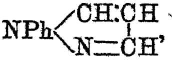
is prepared by the prolonged boiling of phenyldimethylpyrazolecarboxylic acid (Abstr., 1887, 678) with potassium permanganate ($1\frac{1}{2}$ part) in dilute alkaline solution. It crystallises from hot water in small needles, decomposes at 198°, dissolves readily in alcohol and glacial acetic acid, sparingly in ether.

1-*Phenyl*-5-*methylpyrazole*,  $NPh<\begin{matrix}-CMe\\N{:}CH\end{matrix}>CH$, obtained by distilling the dicarboxylic acid, boils at 262° under 754 mm. pressure, and remains liquid at −20°. The *platinochloride*, $(C_{10}H_{10}N_2)_2,H_2PtCl_6 + 2H_2O$, crystallises in long needles, melts at 147°, and decomposes at above 150°.

1-*Phenylpyrazole*-3.4.5-*tricarboxylic acid*,



$$NPh<\begin{matrix}-C(COOH)\\N{:}C(COOH)\end{matrix}>C{\cdot}COOH,$$

is obtained by boiling phenylmethylpyrazoledicarboxylic acid with potassium permanganate ($1\frac{1}{2}$ part) in alkaline solution. It separate from the concentrated ethereal solution in white needles with 1 mo H_2O, melts at 184°, is readily soluble in water, sparingly in chlor form and ether. The *barium salt*, $C_{12}H_6N_2O_6Ba + \frac{1}{2}H_2O$, forn colourless plates. When the acid is distilled, 1-*phenylpyrazole* (?) *ca boxylic acid*, $C_{10}H_8N_2O_2$, is formed. This crystallises in long needle melts at 219—220°, and sublimes in long needles. It dissolves readil in alcohol, rather sparingly in ether and water. When the monocarboxylic acid is heated for a long time in a reflux apparatus, 1-phenylpyrazole,  $NPh\langle\begin{matrix}CH{:}CH\\N = CH\end{matrix},$ is obtained. This distils at 246- under 757 mm. pressure; the *platinochloride*, $(C_9H_8N_2)_2,H_2Pt$ $2H_2O$, crystallises from hydrochloric acid in needles which d pose at 175°. The compound is therefore identical with tha tained by Balbiano from phenylhydrazine and epichlorhydrin.

N. H. M.

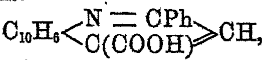
α-Alkylcinchonic Acids and α-Alkylquinolines. By O. Döbner (*Annalen*, **249**, 98—109).—The preparation of the α-alkylcinchonic acids has already been described by the author (Abstr., 1888, 299, and 1887, 504). *Orthohydroxy-α-phenylcinchonic acid*, $C_9NH_5(C_6H_4{\cdot}OH){\cdot}COOH$ [= 2′ : 4′], prepared from aniline, salicaldehyde, and pyruvic acid, crystallises in needles of a brownish-yellow colour. It is freely soluble in alcohol, benzene, acetic acid, and chloroform. The *platinochloride*, $(C_{16}H_{11}NO_3)_2,H_2PtCl_6$, forms golden needles. The acid melts at 238°, and decomposes at a higher temperature, yielding *orthohydroxy-α-phenylquinoline*, $C_{15}H_{11}NO$. The base forms pale-yellow needles. It melts at 115°, and boils above 360°; it is soluble in acids and in alkalis. The *picrate* melts at 184°, and the platinochloride crystallises in needles. In ethereal solution, pyruvic acid, aniline, and cumaldehyde unite together, forming an indifferent compound of the composition $C_{25}H_{24}N_2O$, which melts at 216°, but in alcoholic solution they yield *paraisopropyl-α-phenylcinchonic acid*, $C_{19}H_{17}NO_2$. The acid is deposited from solution in acetic acid or alcohol in yellow plates, and melts at 201°. It is decomposed by heating with soda-lime, yielding *paraisopropyl-α-phenylquinoline*, $C_9NH_6{\cdot}C_6H_4Pr^\beta$. The base crystallises in needles, melts at 60°, and forms a crystalline hydrochloride, dichromate, picrate, and platinochloride. The latter contains 2 mols. H_2O.

α-Phenylquinic acid, $OMe{\cdot}C_9NH_4Ph{\cdot}COOH$ [= 3 : 2′ : 4′], prepared from paranisidine, pyruvic acid, and benzaldehyde, melts at 237°, and dissolves freely in alcohol, forming a fluorescent liquid. The *platinochloride*, $(C_{17}H_{13}NO_3)_2,H_2PtCl_6$, forms orange-red crystals. The acid is decomposed by heat, yielding *α-phenylparamethoxyquinoline*, $C_{16}H_{13}NO$. The base crystallises in plates, and melts at 133°. The hydrochloride, platinochloride, chromate, and picrate are crystalline.

α-Phenylorthomethoxycinchonic acid, [OMe : Ph : COOH = 1 : 2′ : 4′], prepared from orthanisidine, forms needle-shaped crystals of a lemon colour. It melts at 216°, and dissolves in alcohol, forming a feebly fluorescent solution. The *lead salt*, $(C_{17}H_{12}NO_3)_2Pb + H_2O$, is sparingly soluble. The *platinochloride* is crystalline. *α-Phenylorthomethoxyquinoline* is an oily liquid. The *platinochloride*, $(C_{16}H_{13}NO)_2,H_2PtCl_6 + 2H_2O$, and the *chromate* form orange-coloured needles.

W. C. W.

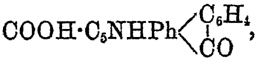
α-Phenylnaphthacinchonic Acids. By O. Döbner and P. Kuntze (*Annalen*, **249**, 109—136).—Pyruvic acid and benzaldehyde act on α- or β-naphthylamine in warm alcoholic or cold ethereal solutions, yielding naphthacinchonic acids.

α-Phenyl-α-naphthacinchonic acid,  $C_{10}H_6<\begin{matrix}N = CPh\\C(COOH)\end{matrix}>CH$, crystallises in yellow needles, and dissolves in acetone, alkalis, chloroform, and also in boiling alcohol and acetic acid. The alcoholic solution exhibits a blue fluorescence. The *sodium salt*, $C_{20}H_{12}NO_2Na + \frac{1}{2}H_2O$, is sparingly soluble in cold water. The potassium and ammonium salts are much more soluble. The zinc, copper, lead, silver, and calcium salts, $(C_{20}H_{12}NO_2)_2Ca$, are insoluble in water. The *ethyl salt* forms long, yellow needles, soluble in alcohol; it melts at 103°. The free acid melts at 300° with decomposition, yielding carbonic anhydride and *α-phenyl-α-naphthaquinoline*; a better yield of the base is obtained by heating the acid or its salts with soda-lime. The base is deposited from a mixture of alcohol and ether in pale-yellow needles melting at 68°. The solution in amyl alcohol is dichroic. The *platinochloride*, $(C_{19}H_{13}N)_2,H_2PtCl_6 + 2H_2O$, is amorphous. The picrate melts at 167°.

Diphenylpyridinetricarboxylic, α-phenylpyridinephenyleneketonecarboxylic, and benzoic acids are the products of the oxidation of α-phenyl-α-naphthacincinchonic acid with a dilute solution of potassium permanganate.

αα'-Diphenylpyridinetricarboxylic acid, $\mathrm{C_5NHPh(COOH)_2{\cdot}C_6H_4{\cdot}COOH}$ [= 2 : 4 : 5 : 6, and 1 : 2], is easily separated from the other product of oxidation by its greater solubility in hot water and in dilute acetic acid. The salts of silver, $\mathrm{C_{20}H_{10}NO_6Ag_3}$, lead, iron, mercury, and copper are insoluble. The acid melts at 250° with decomposition. When heated with soda-lime, it yields 2 : 6-diphenylpyridine, $\mathrm{Ph_2C_5H_3N}$. This base melts at 71—73°, and dissolves freely in alcohol and ether. It yields a crystalline picrate, platinochloride, and chromate.

α-Phenylpyridinephenyleneketonecarboxylic acid,



$$\mathrm{COOH{\cdot}C_5NHPh}\left<\begin{array}{l}\mathrm{C_6H_4}\\ \;| \\ \mathrm{CO}\end{array}\right.,$$

is sparingly soluble in dilute acetic acid and in cold water, but dissolves freely in alcohol and acetone. It crystallises in needles of an orange-red colour, and melts at 226°. Its salts are sparingly soluble. On distillation with soda-lime, α-phenylpyridinephenyleneketone, $\mathrm{CO}\left<\begin{array}{l}\mathrm{C_6H_4}\text{——}\\ \mathrm{C_5NH_2Ph}\end{array}\right>$, melting at 68° is produced.

α-Phenyl-α-naphthaquinoline is converted into tetrahydro-α-phenyl-α-naphthaquinoline, $\mathrm{C_{10}H_6}\left<\begin{array}{l}\mathrm{NH{\cdot}CHPh}\\ \qquad\;\; | \\ \mathrm{CH_2{\cdot}CH_2}\end{array}\right.$, by reduction with tin and hydrochloric acid, or better by the action of sodium on the solution of the naphthaquinoline in amyl alcohol. The hydro-base is a thick syrup boiling above 400°.

α-Phenyl-β-naphthacinchonic acid, $\left.\begin{array}{l}\mathrm{N{\cdot}C_{10}H_6}\diagdown\\ \| \\ \mathrm{CPh{\cdot}CH}\diagup\!\!\diagup\end{array}\right.\mathrm{C{\cdot}COOH}$, is deposited from a mixture of alcohol and hydrochloric acid, or of amyl alcohol and acetic acid, in needles. The acid is also soluble in alkalis, but none of the solutions are fluorescent. The *potassium* salt, $\mathrm{C_{20}H_{12}NO_2K + 5H_2O}$, forms silky needles sparingly soluble in cold water. The *sodium salt* closely resembles the potassium salt. The calcium salt forms needles containing 6 mols. $\mathrm{H_2O}$. On distillation with soda-lime, the acid yields *α-phenyl-β-napthaquinoline*, $\mathrm{C_{10}H_6}\left<\begin{array}{l}\mathrm{N{=}CPh}\\ \qquad | \\ \mathrm{CH{:}CH}\end{array}\right.$. The quinoline forms silky needles or nacreous plates, melts at 188°, and is soluble in alcohol, ether, and benzene. Its salts are partly decomposed by pure water. The *platinochloride*, $\mathrm{(C_{19}H_{13}N)_2,H_2PtCl_6 + H_2O}$, picrate, and dichromate are crystalline. The picrate melts at 250°. The *ethiodide* crystallises in orange-coloured plates, melts at 232°, and is soluble in alcohol. It is reprecipitated from its alcoholic solution by ether. α-Phenyl-β-naphthaquinoline appears to yield a diphenylpyridinedicarboxylic acid on oxidation with potassium permanganate.

W. C. W.

Quinoline-derivatives of Isatinic Acid. By W. PFITZINGER (*J. pr. Chem.* [2], 38, 582—584; compare Abstr., 1886, 370).—The author has obtained α-phenylcinchonic acid by the action of acetophenone on isatinic acid in solution in caustic potash. It is insoluble in water, and crystallises from hot alcohol in slender needles melting at 208—209°. It forms yellow, crystalline salts both with acids and with bases; when distilled with lime, it splits up into carbonic anhydride and α-phenylquinoline; this crystallises from weak alcohol in long needles melting at 84°. This acid has been previously obtained by Döbner (Abstr., 1887, 504) by the interaction of aniline, paraldehyde and pyruvic acid.

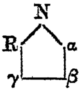
αβ-Diphenylcinchonic acid,

$$C_9NH_4Ph_2{\cdot}COOH\ [Ph_2 : COOH = 2' : 3' : 4']_2,$$

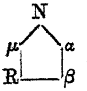
is obtained by the action of deoxybenzoïn on isatinic acid in alkaline solution; it is soluble in hot alcohol, and crystallises in needles which melt at 191°.

Acetone reacts with methylisatin, forming *para-α-dimethylcinchonic acid*, $C_9NH_4Me_2{\cdot}COOH$; this crystallises from water in shining leaflets melting at 261—262°. A. G. B.

Azoles. By A. Hantzsch (*Annalen*, **249**, 1—6).—A purely theoretical paper. The positions of the displaceable hydrogen-atoms in the isazoles are distinguished by the letters α, β, γ, thus:—



, in the azoles by α, β, μ, thus:

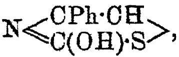


(R = O, S, Se, &c.).

The thiazoles are subdivided into three groups: the true thiazoles, containing the trivalent nucleus $(C_3SN)'''$; the thiazolines or dihydrothiazoles, derivatives of the pentavalent radicle, $(C_3SN)^{v}$; and the heptavalent thiazolidines or tetrahydrothiazoles. The author proposes to substitute the more correct term *thiazylamine* for the name *thiazoline*, which he formerly (Abstr., 1888, 573) suggested for the amidothiazoles. W. C. W.

Conversion of Ketone Thiocyanates into Oxythiazoles, and Reduction of the Latter to Thiazoles. By L. Arapides (*Annalen*, **249**, 7—27).—*Acetophenone thiocyanate*, $COPh{\cdot}CH_2{\cdot}SCN$, is conveniently prepared by mixing alcoholic solutions of barium thiocyanate and bromacetophenone. Barium bromide is deposited, and on evaporating the alcoholic filtrate, acetophenone thiocyanate is left in thick, rhombic prisms. It melts at 74°, and exhibits the characteristic properties of a ketone. It dissolves in strong boiling hydrochloric acid, and the clear solution contains the hydrochloride of carbaminethioacetophenone, $COPh{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}NH_2,HCl$. On the addition of water, the hydrochloride is deposited in silky needles. This salt melts between 175° and 180°, and is soluble in alcohol; it is unstable. The free base cannot be isolated, being transformed into the original acetophenone thiocyanate at the moment of liberation. The platinochloride, $(C_9H_9O_2SN)_2,H_2PtCl_6$, is a pale-yellow, microcrystalline powder, insoluble in alcohol. It decomposes at about 200°.

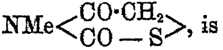
A warm alcoholic solution of carbaminethiacetophene hydrochloride is rapidly converted into *α-phenyl-μ-hydroxythiazole*,

 $N\!<\!\genfrac{}{}{0pt}{}{CPh{\cdot}CH}{C(OH){\cdot}S}\!>$, by the addition of a few drops of hydrochloric acid. The hydroxythiazole is generally prepared by boiling acetophenone thiocyanate with hydrochloric acid until crystals are deposited from the originally clear solution. Phenylhydroxythiazole melts at 204°; it is dissolved by alkalis and reprecipitated by acids. This compound has been already described by Dyckerhoff (this Journal, 1877, ii, 327) as a polymeride of acetophenone thiocyanate.

The hydroxyl in phenylhydroxythiazole can be displaced by chlorine by the action of phosphorus pentachloride. *Phenylchlorothiazole* crystallises in prisms and melts at 98°. The compound is decomposed by warm water with the formation of the hydroxythiazole.

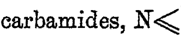
Acetone thiocyanate, $COMe{\cdot}CH_2{\cdot}SCN$, is obtained as an oily liquid by the action of pure monochloracetone on anhydrous barium thiocyanate dissolved in absolute alcohol. It unites with hydroxylamine, forming a stable *acetoxime*, $OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}SCN$, which melts at 135° and dissolves in alcohol. In the presence of hydrochloric acid, acetone thiocyanate is transformed into methylhydroxythiazole; an intermediate product could not be isolated.

The preparation and properties of *α-methylthiazole* have been described by Hantzsch and Arapides (Abstr., 1888, 573). *Phenylthiazole* is also prepared by distilling phenylhydroxythiazole with zinc-dust. It boils at about 271.° W. C. W.

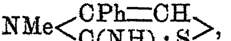
Isothiocyanoacetic Acid. By L. Arapides (*Annalen*, **249**, 27—31).—*ν-Methyl-ψ-dioxythiazole*,  $NMe\!<\!\genfrac{}{}{0pt}{}{CO{\cdot}CH_2}{CO\,-\,S}\!>$, is prepared by digesting dioxythiazole (1 mol.), and sodium methoxide (1 mol.), with excess of methyl iodide and methyl alcohol. It is a deliquescent substance freely soluble in alcohol and water, and is decomposed by boiling with alkalis, yielding carbonic anhydride, thioglycollic acid and methylamine. The formation of methylamine shows that the methyl-group is directly attached to the N-atom. The analogous ν-phenyldioxythiazole has been described by Lange (Abstr., 1880, 44) as diphenylthiocarbamide. Phosphorus pentachloride acts on dioxythiazole, yielding a chloride, $C_3H_3Cl_2NOS$. This compound melts at 161° and decomposes at 170°. The author regards isothiocyanoacetic acid as diketo-thiazolidine. W. C. W.

Amidothiazoles and their Isomerides. By V. Traumann (*Annalen*, **249**, 31—53).—The preparation of mesamidothioazole, or *thiazylamine*, by the action of thiocarbamide on dichlorether, has been described by the author (Abstr., 1888, 573). Thiazylamine crystallises from alcohol in yellow plates, and melts at 90°. It is a monacid base, and forms a crystalline hydrochloride, $C_3SNH_2{\cdot}NH_2,HCl + H_2O$, and platinochloride. The acetyl-derivative melts at 203°, and crystallises in silky needles. *Methylthiazylamine*, prepared from thiocarbamide and monochloracetone, is identical with the compound obtained by Tscherniac and Norton (Abstr., 1883, 568) from ammonium thiocyanate and monochloracetone, and identified by Hantzsch and Weber (Abstr., 1888, 257).

Phenylthiazylamine is deposited from an ethereal solution in yellow prisms, freely soluble in alcohol and ether. It melts at 147°. The hydrochloride and platinochloride are crystalline. The acetic derivative melts at 208°. The existence of diazo-derivatives of thiazylamine, such as thiazolazoresorcinol, has already been mentioned (Abstr., 1888, 573).

The derivatives of thiazylamine are divided into two classes, namely, alkylthiazylamines, obtained by the action of α-chloroketones on monoalkylthiocarbamides,  $N<\substack{CH{=}CH\\ C(NHR)\cdot S}>$, and isoalkylthioazylamines, or *imidoalkylthiazolines*, $NR<\substack{CH{=}CH\\ C(NH)\cdot S}>$, prepared by the action of alkyl chlorides or iodides on mesoamidothiazoles.

α-Methyl-μ-methylamidothiazole, prepared by acting on monochloracetone with methylthiocarbamide, is not identical with, but an isomeride of, α-methylimidomethylthiazoline, described by Hantzsch and Weber (Abstr., 1888, 257). The free base is hygroscopic and melts at 42°. The hydriodide is anhydrous and melts at 136°. The platinochloride crystallises in orange plates and decomposes at 167°. The acetyl-derivative is anhydrous and melts at 110°. The base is decomposed by hydrochloric acid at 220°, yielding methylamine, but the imidomethylthiazoline yields ammonia under similar treatment.

α-Phenyl-μ-methylamidothiazole, prepared from methylthiocarbamide and phenacylbromide, is deposited from ether in large yellow plates, soluble in alcohol. It melts at 138°, and is not decomposed by hydrochloric acid below 138°. The isomeride, *α-phenylmethyl-μ-imidothiazoline*,  $NMe<\substack{CPh{=}CH\\ C(NH)\cdot S}>$, is prepared by the action of methyl iodide on phenylthiazylamine at 110°. It has only been obtained in the form of a syrup, but the hydrochloride is crystalline.

α-Methylthiazylaniline, obtained from phenylthiocarbamide and monochloracetone, crystallises in white needles and melts at 115°. On decomposition with hydrochloric acid, aniline is liberated. *Thiazylaniline*, prepared from dichlorether and phenylthiocarbamide, is deposited from alcohol in white needles. It is freely soluble in alcohol and ether and melts at 126°.

The condensation products of the symmetrical dialkylthiocarbamides with chloracetone, &c., are identical with the so-called dialkylamidothiazoles. The compounds described by Hantzsch and Weber as dialkylamidothiazoles are really *dialkylimidothiazolines*.

Dimethylimidomethylthiazoline, prepared by the action of monochloracetone on dimethylthiocarbamide, is identical with dimethylmethylthiazylamine (Abstr., 1888, 256).

Diphenylimidomethylthiazoline, prepared from monochloracetone and diphenylthiocarbamide, forms yellow prisms soluble in ether. It melts at 138·5°. Attempts to prepare dialkylamidothiazoles, the isomerides of the dialkylimidothiazolines, were unsuccessful.

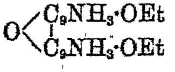
W. C. W.

Isoquinoline. By A. Claus and A. Edinger (*J. pr. Chem.* [2], 38, 491—496).—When an aqueous solution of isoquinoline methiodide (Abstr., 1887, 505) is treated with silver oxide, a strongly alkaline liquid is obtained, containing the corresponding hydroxide, together with another product, from which it may be separated by shaking with ether, which dissolves the bye-product. A crystalline carbonate of this base is formed when carbonic anhydride is passed through its aqueous solution, and from this the platinochloride, $(C_9NH_7Me)_2PtCl_6$, may be obtained in small, lustrous, yellow crystals.

With concentrated aqueous potash, isoquinoline methiodide yields a yellowish-brown oil, insoluble in water, but soluble in other solvents. This base differs from the above in that, (1) its platinochloride, $(C_9NH_6Me)_2,H_2PtCl_6$, does not crystallise; (2) its salts are precipitated by weak ammonia, and (3) it does not form a carbonate.

Papaverine methiodide, $C_{20}H_{21}NO_3,MeI$, crystallises in small, yellow laminæ, which after drying melt at 193—195° (uncorr.). When heated with silver oxide, it gives a base which is soluble in water, forms a carbonate from which other papaverine methyl salts may be formed, and yields a crystalline platinochloride. With potash, a sparingly soluble base is produced, which forms no carbonate, and whose platinochloride does not crystallise. A. G. B.

A Base derived from Diquinoline. By A. COLSON (*Compt. rend.*, **107**, 1003—1005).—A mixture of 7 grams of tetrethoxybenzidine from diethylquinol (Nietzki), 4 grams of orthonitrophenol, and 30 c.c. of sulphuric acid containing one-third of its volume of Nordhausen acid, was gradually heated to 120—125° in a large flask, mixed with 22—25 c.c. of glycerol, and heated to 140—145°. An energetic reaction takes place, and the temperature rises to 190°. After cooling, the product is treated with water, neutralised with sodium carbonate, and extracted with ether. The product crystallises from ether in long, flattened, highly birefractive, white needles, with a slightly bitter taste. It dissolves in six times its weight of dilute hydrochloric acid, and in 10 times its weight of alcohol of 92°, but is only slightly soluble in water, in the vapour of which it volatilises. With concentrated ferric chloride solution, it gives a green coloration; with platinic chloride, it yields a platinochloride, $C_{22}H_{16}N_2O_3,H_2PtCl_6 + 2H_2O$, crystallising in pale yellow crystals, soluble without decomposition in 15 times their weight of boiling water; with auric chloride, it yields a nacreous, deep-yellow aurochloride, insoluble in boiling water. The mode of formation of the base indicates that it is a diethoxydiquinoline base, probably derived from oxydiphenylene,



$$O\left\langle\begin{array}{l}C_9NH_3{\cdot}OEt\\ \,|\\ C_9NH_3{\cdot}OEt\end{array}\right. [OEt : O : C_9N = 1 : 4 : 3].$$

C. H. B.

Alkaloïd from Tea. By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.* [3], **19**, 24).—In the alcoholic extract from 200 grams of Himalayan tea, the authors found no theobromine. After extracting the whole of the theine from the acidified solution by frequent agitation with chloroform, the solution was made alkaline with potash, and again shaken with chloroform. On evaporating this solution, a small quantity of a yellow, amorphous alkaloïd was obtained, which was insoluble in hot water, but soluble in ether, and was therefore neither theïne nor theobromine. The operations are to be repeated with a larger quantity of the tea. The base which Kossel has obtained from tea, to which he has given the name of theophylline, and ascertained to be an isomeride of theobromine, may be identical with this alkaloïd. R. R.

Morphine. By L. Knorr (*Ber.*, **22**, 181—185).—Methylmorphimethine methiodide was treated with silver oxide, and the solution of the ammonium hydroxide evaporated down in a flask connected with a Volhard's receiver containing hydrochloric acid. A thick syrup remained, which when heated at 160° evolved a basic gas in considerable quantity. When the decomposition was complete, the base was completely driven into the acid by a stream of air. The residue in the flask was purified and found to be v. Gerichten and Schrötter's phenanthrene-derivative (Abstr., 1882, 1112). The acid solution contained trimethylamine hydrochloride.

When methylmorphimethine is heated with acetic anhydride at 160—200°, the following compounds are formed:—(1.) Fischer and v. Gerichten's acetylmethyldihydroxyphenanthrene (Abstr., 1886, 563). (2.) An oily *base*, which yields a *methiodide* melting at 295°. (3.) An oily substance, which is not decomposed by water; it can be separated from its aqueous solution by means of potassium carbonate, and distils at 160—186°. (4.) Dimethylamine.

These results show that, of the three carbon atoms in morphine, of which the mode of combination was still unexplained, one is attached to the nitrogen-atom as methyl. Morphine, therefore, cannot contain a pyridine-ring (compare Grimaux, Abstr., 1882, 218; and Hesse, Abstr., 1884, 613). N. H. M.

Water of Crystallisation in Morphine. By O. Hesse (*Pharm. J. Trans.* [3], **19**, 148).—The amount of water found by Dott and by Dietrich in air-dried morphine led them to represent it by the formula $8(C_{17}H_{19}NO_3) + 9(H_2O)$. The author points out that crystalline morphine frequently encloses small quantities of the solvent, which may have vitiated these results. On repeating the determinations with all precautions, values were obtained agreeing very closely with the formula $C_{17}H_{19}NO_3 + H_2O$. R. R.

Narcotine. (Parts III and IV.) By W. Roser (*Annalen*, **249**, 156—168; 168—172).—Methyl iodide acts on cotarnine, yielding a mixture of the hydriodide and of cotarnmethine methiodide. *Cotarnine hydriodide*, $C_{12}H_{13}NO_3,HI$, forms glistening needles, sparingly soluble in cold water and in cold alcohol. Cotarnine melts at 132—133° with decomposition. *Cotarnmethine methiodide*, $C_{11}H_{11}O_4NMe_3I$, forms yellow needle-shaped crystals sparingly soluble in cold water. The *chloride*, $C_{14}H_{20}NO_4Cl + 3H_2O$, and the *platinochloride*, $(C_{14}H_{20}NO_4)_2,PtCl_6$, are also crystalline. The chloride and iodide are decomposed by alkalis, yielding trimethylamine, water, and *cotarnone*, $C_{11}H_{10}O_4$. The conversion of cotarnine into cotarnone leads the author to the following conclusions:—The true formula of cotarnine is $C_{12}H_{15}NO_4$, not $C_{12}H_{13}NO_3 + H_2O$. Cotarnine is a secondary base. The salts of cotarnine contain the pyridine-ring, but the free base does not.

Cotarnone dissolves freely in alcohol, ether, and acetic acid, and melts at 78°; it is an indifferent substance, with ketone-like properties. *Cotarnonoxime*, $C_{10}H_{11}O_3\!:\!NOH$, melts with decomposition about 130—132°. *Cotarnic acid*, $C_8H_6O_3(COOH)_2$, prepared by the oxidation of cotarnone with potassium permanganate, crystallises in plates and melts at 178° with decomposition, yielding the anhydride which melts at 161—162°. The salts of barium, $C_{10}H_6O_7Ba$, potassium, $C_{10}H_7O_7K + 2\frac{1}{2}H_2O$, and silver, $C_{10}H_6O_7Ag_2$, are crystalline.

The action of methyl iodide on hydrastinine is analogous to its action on cotarnine; a volatile base and an indifferent substance being formed; the latter is a viscid oil which yields an oxime melting at 129°.

The constitution of cotarnine and its derivatives as deduced from the results of these experiments and previous researches, can be represented by the following formulæ:—

Cotarnine, a secondary base and an aldehyde—

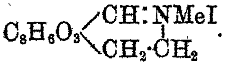
$$CHO\cdot C_8H_6O_3\cdot CH_2\cdot CH_2\cdot NHMe.$$

Cotarnmethine methiodide, $CHO\cdot C_8H_6O_3\cdot CH_2\cdot CH_2\cdot NMe_3I$.

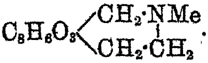
Cotarnone, $CHO\cdot C_8H_6O_3\cdot CH\!:\!CH_2$.

Cotarnonoxime, $OH\cdot N\!:\!CH\cdot C_8H_6O_3\cdot CH\!:\!CH_2$.

Cotarnic acid, $C_8H_6O_3(COOH)_2$.

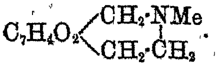
Cotarnine iodide, 

$$C_8H_6O_3\left\langle\begin{array}{l}CH\!:\!NMeI\\ CH_2\cdot CH_2\end{array}\right..$$

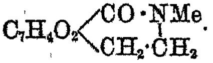
Hydrocotarnine, 

$$C_8H_6O_3\left\langle\begin{array}{l}CH_2\cdot NMe\\ CH_2\cdot CH_2\end{array}\right..$$

Hydrastinine, $CHO\cdot C_7H_4O_2\cdot CH_2\cdot CH_2\cdot NHMe$.

Hydrohydrastinine, 

$$C_7H_4O_2\left\langle\begin{array}{l}CH_2\cdot NMe\\ CH_2\cdot CH_2\end{array}\right..$$

Oxyhydrastinine, 

$$C_7H_4O_2\left\langle\begin{array}{l}CO\cdot NMe\\ CH_2\cdot CH_2\end{array}\right..$$

W. C. W.

Additive Compound of Papaverine with Phenacyl Bromide. By E. v. SEUTTER (*Monatsh.*, 9, 1035—1044).—When a finely-powdered mixture of papaverine (10 grams) and phenacyl bromide (6 grams) is heated for three hours at 70—80°, the colourless mass melts to form a reddish-yellow oil which solidifies to a yellow crystalline mass; this, on recrystallisation from much hot water, furnishes fan-shaped groups of pyramids of the formula $C_{20}H_{21}NO_4,COPh\cdot CH_2Br + 2\frac{1}{2}H_2O$. This compound loses $1\frac{1}{2}$ mols. of water on exposure to the air, and is rendered anhydrous when heated at 110°. It is insoluble in cold water and in cold alcohol, dissolves readily in chloroform and carbon bisulphide, blackens at 190°, and decomposes rapidly at 194°. It dissolves in concentrated sulphuric acid, forming a beautiful carmine-red solution.

Papaverine phenacyl nitrate, $C_{20}H_{21}NO_4,COPh{\cdot}CH_2{\cdot}NO_3 + 2H_2O$, is insoluble in cold water, slightly soluble in hot water and alcohol, and decomposes at 173°. The *picrate* crystallises from hot alcohol in silky needles, softening at 180°, and melting at 182° with previous blackening. It is almost insoluble in cold water and cold alcohol. The *dichromate* crystallises in short needles, the *chloride* in long needles, and the *platinochloride* is only slightly soluble in boiling water.

When a solution of papaverine phenacyl bromide is decomposed with a dilute solution of sodium hydroxide, an orange-red precipitate forms which appears to have the formula $C_{20}H_{21}NO_4,COPh{\cdot}CH_2{\cdot}OH$; this, on warming to 80° or on recrystallising from hot alcohol, loses water and is converted into *papaverine phenacyl oxide*, $(C_{20}H_{21}NO_4,COPh{\cdot}CH_2)_2O$, which crystallises in needles, is insoluble in water and ether, but dissolves in alcohol, benzene, chloroform, and carbon bisulphide; it softens at 180°, and melts at 186—187°. The alcoholic solution has a splendid violet-blue fluorescence. This base can also be obtained by boiling papaverine phenacyl bromide for a long time with much water. G. T. M.

Cocaïnes. By C. LIEBERMANN (*Ber.*, **22**, 130—133).—*ε-Isatropylcocaïne*, $C_{19}H_{23}NO_4$, is obtained by heating ecgonine (2 parts), water (1 part), and γ-isatropic anhydride (2 parts) on a water-bath for three hours. The product is extracted with water, dried, dissolved in a little methyl alcohol, and the solution saturated with hydrogen chloride, and kept over night. It is then filtered, and the solution evaporated in a partial vacuum over lime and sulphuric acid. The residue is treated with water, extracted with ether, and the solution precipitated by means of sodium carbonate. The compound thus prepared has all the properties of the natural isatropylcocaïne. The two compounds are, however, not identical. When the substance, prepared as above, is decomposed it does not yield γ-isatropic acid (m. p. 274°), but ε-isatropic acid (m. p. 228°).

Anisylecgonine, $C_8H_7O_2{\cdot}C_9H_{14}NO_3$, obtained from ecgonine, anisic anhydride, and water, crystallises from alcohol in colourless needles melting at 194°.

Anisylcocaïne, is a viscous substance insoluble in water. The *aurochloride*, $C_8H_7O_2{\cdot}C_9H_{14}MeNO_3,HAuCl_4$, is yellow; it is insoluble in water and dilute alcohol.

Cinnamylcocaïne forms small, colourless, monoclinic prisms; $a : b : c = 0{\cdot}8616 : 1 : 0{\cdot}8479$; $\beta = 84° 20'$. N. H. M.

Cinnamic Acid in the Product of Decomposition of Crude Cocaïne. By H. FRANKFELD (*Ber.*, **22**, 133—134).—The crude material was extracted with water, treated with cold, dilute alkali, and the residue boiled with alkali; it contained cinnamic, γ- and δ-isatropic acids, and a trace of benzoic acid. N. H. M.

A Metameric Cocaïne and its Homologues. By A. EINHORN (*Ber.*, 21, 3441—3443).—*Methyl cocaylbenzoylhydroxyacetate*, $C_5H_7NMe\cdot C(OH)(COPh)\cdot COOMe$, prepared by passing hydrogen chloride into an alcoholic solution of the acid (compare this vol., p. 169), is a colourless oil. The *hydrochloride*, *hydrobromide*, and the sparingly soluble *hydriodide*, $C_{16}H_{19}NO_4,HI$, crystallise in needles. The *ethyl* salt is a colourless oil; the *hydrochloride* and the *hydrobromide* crystallise in needles; the sparingly soluble *hydriodide* crystallises in prisms. The *propyl* salt crystallises in slender needles, melts at 56—58°, and is very readily soluble in most of the ordinary solvents, but insoluble in water. The *hydrochloride*, $C_{18}H_{23}NO_4,HCl$, *hydrobromide*, and *hydriodide* crystallise in needles. F. S. K.

Alkaloïds of Areca-nut. By E. JAHNS (*Ber.*, 21, 3404—3409).—The bases contained in areca- or betel-nut can be isolated by either of the following methods:—

(1.) The crushed seeds (1 kilo.) are extracted three times with cold water containing 2 grams of concentrated sulphuric acid, the filtered solution concentrated to about 1 litre, and the cold and filtered solution precipitated with potassium bismuth iodide and sulphuric acid. The red, crystalline precipitate, which is soluble in excess of the reagent, is separated after some days, washed, and decomposed by boiling with barium carbonate and water. The filtered and concentrated solution is mixed with barium oxide, and the oily alkaloïd, which the author names arecoline, extracted with ether. The residual mixture is neutralised with sulphuric acid, and the filtered solution is treated consecutively with silver sulphate, barium oxalate, and carbonic anhydride. The solution of the bases is evaporated to dryness, and the residue extracted with cold absolute alcohol or chloroform; an alkaloïd, which the author names arecaïne, remains, and a third alkaloïd, together with colouring matters, &c., are dissolved, and are obtained as an amorphous mass when the solution is evaporated.

(2.) The crushed seeds are treated with cold milk of lime, the filtered extract is neutralised with sulphuric acid, evaporated to a syrupy consistency and then diluted with a small quantity of water; after concentrating the filtered solution and adding alkali, the arecoline is extracted with ether and the other bases are isolated as described above. The yield of arecoline is 0·07—0·1 per cent., that of arecaïne is about 0·1 per cent.; the third base is obtained in very small quantities.

Arecoline, $C_8H_{13}NO_2$, is obtained in the pure state by shaking the ethereal extract (see above) with dilute acid, concentrating the neutralised solution, and, after adding alkali, extracting the alkaloïd with ether. The base is neutralised with hydrobromic acid, the salt is repeatedly recrystallised from absolute alcohol, and the alkaloïd is then obtained by decomposing the pure hydrobromide with alkali. It is a colourless, oily liquid, with a strongly alkaline reaction, and is miscible with water, alcohol, ether, and chloroform in all proportions. It seems to boil at about 220°. The salts are readily soluble and, although some are deliquescent, they are mostly crystalline. Potassium bismuth iodide gives a garnet-red, and phosphomolybdic acid a white precipitate in solutions of the salts. Potassium mercuric iodide, solutions of iodine, picric acid, and auric chloride produce oily precipitates, which, as a rule, crystallise after some time, but platinic chloride, mercuric chloride, and tannic acid give no precipitation.

The *hydrobromide*, $C_8H_{13}NO_2,HBr$, crystallises in prisms, melts at 167—168°, and is readily soluble in water. The *hydrochloride* crystallises in slender, deliquescent needles, and is readily soluble in alcohol or in a mixture of alcohol and ether; it seems to form several double salts with cadmium chloride. The *sulphate*, *acetate*, and *nitrate* resemble the hydrochloride. The *aurochloride*, $C_8H_{13}NO_2,HAuCl_4$, is a yellow oil, and is sparingly soluble in cold water. The *platinochloride*, $(C_8H_{13}NO_2)_2,H_2PtCl_6$, separates in flocks when ether is added to an alcoholic solution of the hydrochloride and platinic chloride, and, after washing with alcoholic ether, it separates from water in orange-red, rhombic crystals, melting at 176° with decomposition.

Arecoline is a powerful poison, and is doubtless the active physiological constituent of areca-nut.

Arecaïne, $C_7H_{11}NO_2 + H_2O$, is purified by repeatedly recrystallising from 60 per cent. alcohol. It is colourless, and is readily soluble in water and dilute alcohol, but almost insoluble in absolute alcohol, ether, chloroform, and benzene. It loses its water at 100° and melts at 213° with decomposition. It has no apparent physiological action. Potassium bismuth iodide, when added to a dilute sulphuric acid solution, produces a red, amorphous precipitate, which soon becomes crystalline; potassium mercuric iodide gives a yellow, crystalline precipitate under the same conditions. Potassium iodide gives a dark, crystalline precipitate in dilute acid solutions, but phosphomolybdic acid and tannin only produce a slight turbidity, whilst picric acid causes no precipitation. The *hydrochloride*, $C_7H_{11}NO_2,HCl$, the *aurochloride*, $C_7H_{11}NO_2,HAuCl_4$, melting at 186—187°, and the *platinochloride*, $(C_7H_{11}NO_2)_2,H_2PtCl_6$, melting at 213—214° with decomposition, are crystalline.

The third alkaloïd referred to above is an amorphous, strongly alkaline base; it is readily soluble in water, alcohol, and chloroform, but only sparingly in ether. The *platinochloride* crystallises in prisms or plates. F. S. K.

Ptomaïnes. By O. DE CONINCK (*Compt. rend.*, **108**, 58—59).—When the alkaloïd obtained from the cuttle-fish (Abstr., 1888, 730, 1118) is oxidised with dilute potassium permanganate solution, it yields a gummy acid, which in concentrated solutions gives a bulky, pale-blue precipitate with cupric acetate. This acid is almost insoluble in cold water, but dissolves readily in warm water and in alcohol. It melts at 220—228°, and when distilled with calcium oxide, it yields pyridine. The properties of the acid very closely resemble those of nicotinic acid. These results confirm the author's view that this base is a ptomaïne of the pyridine series. C. H. B.

Ptomaïnes and their Genesis, in relation to Panum's Sepsin. By J. M. WYBORN (*Chem. News*, **59**, 2).—As it seems probable that in many cases where ptomaïnes have been attributed to putrefaction, they may really have been produced by the action of acids on lecithin and albuminoïds, the author has made experiments avoiding the use of acids.

Finely minced beef was macerated with twice its weight of water and exposed to the heat and light of the sun for 16 days, free access of air being prevented. The strained liquor was precipitated with an equal bulk of absolute alcohol, the precipitate boiled with the same quantity of alcohol, washed with boiling alcohol, and dried in warm air. It was then treated with water, filtered, and evaporated to dryness. The residue from the evaporation, amounting to 0·067 per cent. of the beef used, consisted of:—1. A heavy brownish-red matter freely soluble in water; 2. A very light, pale-greenish substance, sparingly soluble; and 3. Brilliant, white, crystalline plates. With a mixture of equal volumes of glycerol and water, it yielded an amber-coloured solution and a brown precipitate; the solution was at first nearly neutral, but after exposure to the air became acid, and acquired the odour of stale pepsin. After keeping a month, 5 or 6 minims, containing $\frac{1}{16}$ grain of residue, injected under the skin, proved fatal to mice in about an hour. Reactions with various reagents indicate the presence of peptones and cadaveric alkaloïds, and "unless the alcohol were alone sufficient to produce them (the latter) in the putrid solution, their pre-existence may be reasonably inferred." D. A. L.

Acids of Pig's Bile. By S. JOLIN (*Zeit. physiol. Chem.*, **13**, 205—247).—A further contribution relating to the acids of pig's bile (see Abstr., 1888, 1213). Various metallic compounds (with sodium, potassium, lead, magnesium, copper, &c.) of the α- and β-hyoglycocholic acids were prepared and analysed. The following conclusions were arrived at: the α-acid is precipitated by dilute acids more easily than the β-acid. The salts of the alkalis are less soluble in water in the case of the α-acid, and are more easily precipitated by saturated salt solutions. The barium, calcium, and magnesium salts of the α-acid do not dissolve in excess of the bile salt, like those of the β-acid, but form a flocculent or granular, not a sticky precipitate. The salts of the α-acid with the heavy metals do not fuse on heating the solution like those of the β-acid. The sodium salt of the α-acid dissolved in water is optically inactive, that of the β-acid, dextrorotatory. The alkaline salts of the α-acid are bitter to the taste, whilst those of the β-acid are first sweet then bitter.

Further experiments were performed to ascertain correctly the proportion of various neutral salts necessary to cause precipitation of the sodium salts of the two acids. The salts investigated were sodium chloride, sulphate, nitrate, and potassium nitrate. The hyocholic acids prepared from the two acids were very much alike, but not identical, the differences consisting chiefly in the amount of neutral salt (sodium chloride, sulphate, potassium nitrate) necessary to cause precipitation of the sodium hyocholate; the salt of the α-hyocholic acid being precipitated more easily than that of the β-acid. The barium and silver salts were also prepared, analysed, and their reactions described.

W. D. H.

Elastin and Elastoses. By R. H. CHITTENDEN and A. S. HART (*Zeit. Biol.*, **25**, 368—389).—Horbaczewski (Abstr., 1887, 270) observed that elastin is digested by gastric juice. The final product is a peptone, and the intermediate substances he named hemielastin. In the present research, elastin was prepared from the ligamenta nuchæ of the ox, soluble substances being removed by prolonged extraction with hot water, potash, acetic acid, and alcohol. In the elementary analyses of this substance sulphur was not found. In another specimen, in which the extraction with potash was omitted, a small percentage of sulphur (0·3) was found. It is doubtful, however, whether this is contained in the elastin molecule or in proteïd matter mixed with it; the authors incline to the former view.

The elastin was subjected to treatment with boiling water, to which a trace of hydrochloric acid had been added; another portion to artificial gastric digestion, and a third portion to artificial pancreatic digestion. In all three cases, two products were obtained, which are named *protoelastose* and *deuteroelastose*, terms symmetrical with those of the corresponding proteoses. No trace of any hetero-product was found; the protoelastose has the characters and composition of Horbaczewski's hemielastin. The question whether true peptone is formed on energetic digestion has yet to be investigated. The original paper gives full details of the separation, reactions, and analysis of these substances. W. D. H.

Myosin and Myosinoses. By W. KÜHNE and R. H. CHITTENDEN (*Zeit. Biol.*, **25**, 358—367).—The primary products of digestion of fibrin, egg albumin, globulin, caseïn and vitellin have been previously studied; the ultimate product is peptone, and the intermediate substances, albumoses, globuloses, &c., may be conveniently included under the generic term proteoses. The present paper relates to the proteoses obtained in the digestion of myosin.

Myosin was extracted from muscles by the use of ammonium chloride solutions; from such extracts, the myosin was precipitated in a gelatinous form by dialysing away the salts, it was then submitted to elementary analysis. Some was submitted to gastric digestion, and then the insoluble residue to pancreatic digestion. But in the latter case, the formation of peptone was so rapid that no myosinoses were obtainable. In the case of gastric digestion, however, considerable quantities of proto- and deutero-myosinose were obtained, but only small quantities of heteromyosinose. These products were separated from one another by the methods the authors have already described in the case of other proteoses.

Protomyosinose only differs from protoalbumose in its reactions, in that nitric acid does not precipitate it from solutions free from salt. *Deuteromyosinose*, like deuteroalbumose, is not precipitated by copper sulphate in the cold; after boiling and subsequent cooling, however, a precipitate forms. It is precipitated by saturation with salts, but with greater difficulty than deuteroalbumose is. Both these albumoses in an aqueous solution are alkaline in reaction. The following table contrasts their percentage composition with that of myosin.

	Myosin.	Protomyosinose.	Deuteromyosinose.
C	52·79	52·43	50·97
H	7·12	7·17	7·42
N	16·86	16·92	17·00
S	1·26	1·32	1·22
O	21·97	22·16	23·39

W. D. H.

Artificially prepared Nucleïns. By J. Pohl (*Zeit. physiol. Chem.*, **13**, 292—297).—Liebermann (Abstr., 1888, 510) has shown that a substance having the properties of nucleïn may be artificially prepared from metaphosphoric acid and white of egg. White of egg contains, however, at least two proteïds (globulin and albumin) and the present research relates to nucleïn prepared artificially from pure proteïds; namely, (1) serum albumin freed from globulin by magnesium sulphate; and (2) varieties of albumose obtained by the fractional precipitation of a solution of commercial peptone by ammonium sulphate. Nucleïn from serum albumin so prepared contains about 5·5 per cent. of phosphorus; from one variety of albumose, 4·8; from another, 6·5. Although these artificial nucleïns resemble native nucleïn in their solubilities, they differ from it in the fact that substances of the uric acid group (xanthine and hypoxanthine) cannot be obtained from them on decomposition. These substances also do not form insoluble compounds with metaphosphoric acid. Guanidine hydrochloride, however, gives with sodium metaphosphate a crystalline precipitate which contains 22·3 per cent. of phosphorus; thus corresponding with the formula CN_3H_5,HPO_3. Certain vegetable bases (strychnine nitrate, quinine hydrochloride) form similar compounds.

W. D. H.

Action of Salts on the Proteïds of Serum. By S. Lewith (*Arch. exper. Path. Pharm.*, **24**, 1—16).—These experiments are similar to those of Kauder with ammonium sulphate (*Arch. exper. Path. Pharm.*, **20**, 411), who determined the amount of that salt necessary to precipitate the globulin and albumin of serum. Halliburton (*J. Physiol.*, **5**, 152) has made similar experiments, although not quantitative ones, with a large number of different salts. Salts which were found to produce no precipitation of the proteïds even when added to saturation were potassium sulphate, nitrate, and chlorate; ammonium chloride, nitrate, and acetate; calcium acetate; barium chloride, nitrate, and acetate; magnesium chloride, nitrate, and acetate. Those which were found to produce a greater of less precipitation were potassium chloride and acetate; sodium chloride, sulphate, nitrate, chlorate, phosphate, and acetate; calcium chloride and nitrate; magnesium sulphate. With three of these salts, Halliburton obtained, however, negative results, namely, potassium chloride, sodium sulphate, and sodium phosphate. In the present research, a somewhat higher temperature was used than in Halliburton's work, and this probably accounts for the discrepancy: the precipitate produced was, however, small in all three cases.

The following table gives the results of the quantitative estimation of the amount of salt necessary to produce precipitation of the two proteïds of serum:—

Salt.	Percentage of salt necessary to produce				Result of saturation.
	Precipitation of globulin.		Precipitation of albumin.		
	Begins.	Ends.	Begins.	Ends.	
Sodium sulphate	11·4	—	—	—	Incomplete precipitation of globulin.
Ammonium sulphate	14·2	23·1	33·6	47·2	Complete precipitation of both.
Sodium acetate	14·6—15	—	—	—	Nearly complete precipitation of globulin.
Sodium nitrate	43—46	—	—	—	Do. do.
Magnesium sulphate	16·9	25·7	—	—	Complete precipitation of globulin.
Potassium acetate	17—22	35·2	64·6	88·1	Complete precipitation of both.
Sodium chloride	21·8	—	—	—	Incomplete precipitation of globulin.
Potassium chloride	25·9	—	—	—	Do. do.

The solubility of the salts is by no means parallel to the power they have in precipitating the proteïds. The sulphates and acetates seem to be the most powerful in this direction, then the chlorides, and lastly the nitrates.

W. D. H.

Action of Salts on Proteïds. By F. Hofmeister (*Arch. exper. Path. Pharm.*, **24**, 247—260).—This is a research of similar nature to that of Lewith (see preceding Abstract). Instead of using serum, however, a solution of globulin prepared from white of egg was employed; and all observations were made using the same strength of globulin solution, in order to compare them more justly with one another. Lewith used serum containing very varying percentages of globulin and albumin. The number of salts employed was very numerous, and the results are given in tabular form similar to that quoted in the preceding Abstract. The salts are then arranged in groups according to certain properties; and it is found (although not without exceptions) that purgative power, difficulty of diffusion, and power of precipitating globulins go together.

W. D. H.

Physiological Chemistry.

Can the Mucous Membrane of the Stomach decompose Bromides and Iodides? By E. DRECHSEL (*Zeit. Biol.*, 25, 396—399).—Külz (Abstr., 1887, 508) has found by Rabuteau's (quinine) method of separating the free acid in gastric juice that he obtains quinine hydrochloride: in artificial gastric juice to which the bromides of the alkali metals had been added, that quinine hydrobromide was also formed, and in experiments on dogs he also considered he had proved the existence of free hydrobromic or hydriodic acids in the gastric juice after the administration of a bromide or iodide respectively. But there is a factor in the case which he overlooked, and that therefore renders his deductions invalid: this is the old question, how many salts are contained in a solution formed by mixing solutions of two salts with different bases and acids? When equivalent quantities of solutions of such salts as mercuric chloride and sodium nitrate are mixed, doubtless there are only two salts in the mixture; but in other cases there would be four salts: chlorides and nitrates of both metals.

So in a mixture of sodium bromide and free hydrochloric acid, there would also be sodium chloride and free hydrobromic acid; and hence in a simple mixture like this, by treatment with quinine the hydrobromide and the hydrochloride of that alkaloïd would both be formed. Hence the action of the gastric mucous membrane is not necessarily proved to be that of bringing about a decomposition of the molecules of the bromide or iodide used.

This theoretical objection to Külz's conclusions was put to the test of experiment, and it was found that hydrobromic and hydriodic acids could be recognised by treating mixtures of either the bromide or iodide of potassium or sodium and weak hydrochloric acid with quinine as in Rabuteau's method. The question raised by Külz is therefore still unanswered. W. D. H.

Tension of Oxygen in Blood and in Solutions of Oxyhæmoglobin. By G. HÜFNER (*Zeit. physiol. Chem.*, 13, 285—291); compare Abstr., 1888, 1214).—One point not worked out in the earlier research is the influence of the concentration of the oxyhæmoglobin solution in the dissociation that takes place. The following table illustrates the results now obtained bearing on this point as well as the influence of fever temperature; t, p, and v represent respectively temperature, pressure, and volume of oxygen before, and t' p', and v' after the shaking.

The limiting pressure of dissociation is thus higher at this temperature than in the previous research. In researches 4 and 5 the initial pressure was lower than in the others. The last four researches illustrate the effect of concentration. The solution with higher concentration still gives off oxygen, whilst one of half the concentration and at about the same temperature does not.

	Percentage of oxyhæmoglobin.	t.	t'.	$p'-p$.	$v'-v$.
1.	11·06	39°·0	38°·5	1·13	0·31
2.	11·06	39·0	38·5	1·58	0·41
3.	12·97	39·0	38·3	0·13	0·09
4.	16·51	39·1	38·5	11·16	2·67
5.	16·51	39·4	38·9	10·31	2·47
6.	16·63	40·0	39·25	0·97	0·33
7.	8·32	39·6	39·1	−0·80	−0·15
8.	16·84	39·25	38·7	1·16	0·35
9.	8·42	39·7	39·1	−0·10	0·01

If one can apply results obtained with solutions of oxyhæmoglobin outside the body to the solving of problems occurring in the red corpuscles of the blood, the best means of rendering breathing possible in high altitudes would be to increase the richness of the blood in hæmoglobin. W. D. H.

Blood Tablets and Thrombosis. By M. Löwit (*Arch. exp. Path. Pharm.*, **24**, 188—220).—The blood tablets of mammalian blood seem to be absent from the blood of birds, amphibians, reptiles, and fishes. By certain methods of microscopical staining with gentian violet, which are fully described, it is found that the fibrin network and the blood tablets stain similarly, whilst the white blood corpuscles remain unaffected or are only lightly stained. The tablets are therefore regarded as a most important precursor of fibrin, and are considered to consist chiefly of a globulin which is readily changed into or takes part in the formation of fibrin. The colourless plugs sometimes found in veins (thrombi) are also considered to be chiefly composed of blood tablets. The spindle cells of the blood of Batrachians and birds are not the equivalent of blood tablets, as some have supposed (Eberth and Schimmelbusch, *Virchow's Arch.*, **108**, 36[illegible]), but are merely varieties of white blood corpuscles. W. D. H.

Influence of Starvation on the Glycogen of the Liver and Muscle. By G. Aldehoff (*Zeit. Biol.*, **25**, 137—162).—The question has been investigated by others previously, and references to their work are given. It was judged necessary to reopen the question, as in the previous work on the subject the method of Külz (Abstr., 1887, 494) had not been employed. This is a method which is believed to give more trustworthy results from a quantitative point of view than any other. Experiments were made on frogs, rabbits, cats, horses, pigeons, and fowls. The quantitative results are given in tabular form, and the following are the general conclusions that are drawn:—

In the fowl, the glycogen, under the influence of starvation, disappears not only in the heart muscles but also in the muscles of the limbs and other parts, much more slowly than in the liver. This is opposed to Luchsinger's statement (*Dissert.*, *Zurich*, 1875) that the heart muscles are richer in glycogen during inanition than those of the limbs and other parts of the body; but agrees with the statement of Weiss, that the muscle-glycogen does not disappear so quickly as that in the liver, when insufficient carbohydrate food is given; the same statement holds for most of the other animals (pigeons, rabbits, cats, and horses) used in the research. The muscle-glycogen of summer and winter frogs remains fairly constant during inanition, or varies within narrow limits; the glycogen of the liver, however, disappears much more quickly in summer frogs than in winter frogs; in the latter, after abstinence from food for two months, relatively large quantities of glycogen are still to be found in the liver.

In the hearts of two horses, after a nine days' fast, 0·82 and 0·58 per cent. of glycogen respectively was found; and in a cat which had been without food for a fortnight, the heart still contained 0·44 per cent. of glycogen. In the skeletal muscles of the horse, larger percentages still were found (0·098—1·34).

Luchsinger considers that glycogen is not the direct source of energy in contracting muscle, but this is in no way proved by his researches, for it is doubtful whether he could ever have obtained muscles free from glycogen. Estimations of glycogen by weighing and by the polarimetric method correspond with one another very well.

W. D. H.

Effect of Muscular Work on the Glycogen in the Muscles. By E. MANCHÉ (*Zeit. Biol.*, 25, 163—179).—Weiss (*Sitzb. d. k. Akad. der Wissensch.*, Abth. 64) stated that on contraction the amount of glycogen in the muscles diminishes. Weiss used Brücke's method of estimating the glycogen: this is a method which does not give such good results as that of Külz; for this reason, among others, it was deemed advisable to repeat the experiments. In the present research, Külz's method of estimating the glycogen was used. The experiments were performed on frogs, and the following table illustrates the results obtained:—

	Weight of glycogen in limb at rest.	Weight of glycogen in limb which was made to contract from 23—65 minutes.	Loss of glycogen per cent. in tetanised limbs.
	gram.	gram.	
1........	0·1277	0·1114	12·76
2........	0·2287	0·1942	15·09
3........	0·2267	0·1917	15·44

In other words, the limbs which were stimulated to contract, lost from 12 to 15 per cent. of their glycogen in an hour, and thus Weiss's statement was confirmed.

Chandelon (*Pflüger's Archiv*, 13, 626) came to the conclusion that section of the nerve of a muscle caused an increase in the glycogen of the muscle. These experiments were repeated on rabbits, using Külz's method of analysis as before; the following table illustrates the results obtained:—

	Operation of cutting one sciatic nerve performed.	Increase (per cent.) of glycogen on operated side as compared with the normal.
1	5 days before death	6·25
2	7 " "	26·67
3	20 " "	33·33
4	2 " "	8·33
5	2 " "	10·00

As Chandelon states, the paralysed muscles contained a greater quantity of glycogen; this is probably explained by the fact that the intact muscles of the other limb had been contracting since the operation, and thus the glycogen in them was lessened.

Other experiments of Chandelon's were also repeated and fully confirmed; namely, those which illustrate the fact that ligature of the artery supplying a muscle leads to a decrease of its glycogen. The loss of glycogen was greatest in those cases where œdema followed the operation; the saturation of the tissues by lymph leads probably to saccharification. W. D. H.

Source of the Glycogen of Muscle. By C. Schmelz (*Zeit. Biol.*, **24**, 180—207).—This research, like those related in the two preceding Abstracts, consisted mainly of a repetition of the work of previous investigators. Various criticisms are passed on the methods adopted by them; and the estimations in the present experiments were made by Külz's method, or by the polarimeter (Cramer, *Zeit. Biol.*, **24**, 67); these two methods giving approximately equal results. The net result of the experiments, however, is merely to confirm the results arrived at by Brücke's seemingly less exact method.

Minkowski (*Arch. f. exp. Path. Pharm.*, **23**, 139) and Laves (*Inaug. Dissert.*, *Königsberg*, 1886) stated that after extirpation of the liver, the amount of glycogen in the muscles markedly diminishes; they consider that the muscular glycogen chiefly originates in the liver. This diminution was also found to be the case in the present research; moreover, feeding on cane-sugar produced no marked increase of the muscle-glycogen either in normal animals or in those in which the liver had been removed. W. D. H.

Secretion of Lime by Animals. By R. Irvine and G. Sims Woodhead (*Proc. Roy. Soc. Edin.*, **127**, 308—316).—Dana and J. Y. Buchanan have stated their belief that the calcium carbonate excreted by polyps, &c., is absorbed as sulphate, and converted first into sulphide and then to carbonate. The authors, therefore, experimented with fowls, shutting them up so that they could obtain no lime other than that given to them as sulphate—the hens continued to lay eggs with normal shells. They also show that fowls are unable to store up in their gizzard more lime as carbonate than is sufficient for the formation of the shells of two or three eggs, and that if lime is not procurable, either they will lay soft eggs, or will cease to lay; there is also a discussion as to the various parts of the bird which take part in the excretion of lime. E. W. P.

Proteïds in Milk. By J. SEBELIEN (*Zeit. physiol. Chem.*, **13**, 135—180).—See p. 450.

Guanine in the Excrement of Spiders. By C. WEINLAND (*Zeit. Biol.*, **25**, 390—395).—Will and Gorup-Besanez have described guanine in the excrement of the spider, in the organ of Bojanus of the mussel, and in the green glands of the crayfish. Voit was not able to find it in the organ of Bojanus, but he found it in the flesh of pigs, and also in the swimming-bladder of the *Argentina sphyræna.* The present research is concerned with spiders; the excrement was collected and found to consist of roundish particles 4—10 mm. across, and of a reddish-yellow colour. From this, crystals of guanine were prepared which gave the reactions of that substance as described by Capranica (*Zeit. physiol. Chem.*, **4**, 233). W. D. H.

Cystin. By RADZIWILLOWICZ (*Chem. Centr.*, 1888, 1415, from *Berlin. klin. Wochensch.*, **25**, 835—836).—In order to separate cystin from animal excreta, the author recommends extraction of the strongly ammoniacal liquid with amyl alcohol, evaporation and treatment of the residue with water. He thus isolated 0·1 milligram from 2 c.c. of solution, and confirmed its presence with potassium mercuric iodide, iodine in potassium iodide or phosphotungstic acid. Its toxicological action appears to be qualitatively the same with all animals, although differing in degree, not only with the different species but also with different members of the same species. Spectroscopical investigation shows that blood impregnated with cystin remained longer arterial, and its action appears to tend to the suppression of consumption of oxygen in the system. J. W. L.

Relation between the Total Sulphuric Acid of the Urine and that Existing as Ethereal Sulphates in Rest and Work. By S. SHER (*Diss. for M.D. St. Petersburg*, No. 4, 1888—1889).—The total sulphuric acid (*a*) and that existing in the form of ethereal sulphates (*b*) in the urine of 26 persons of different classes (doctors, soldiers, prisoners, peasants, &c.), was estimated by day and by night, in work and at rest. It was found that *a* was less during rest than during work, that *b* was also less during rest, and that the ratio between *a* and *b* was less during rest than during work.

Exceptions to these rules occurred when the work was excessive and exhausting. The mean quantities obtained were as follows:—REST by day, *a* 1·4128, *b* 0·1733, ratio 8·1; by night, *a* 1·3343, *b* 0·1601, ratio 8·3; during the 24 hours, *a* 2·7471, *b* 0·3334, ratio 8·2.

WORK by day, *a* 1·6176, *b* 0·1803, ratio 8·9; by night, *a* 1·3556, *b* 0·1408, ratio 9·6; during the 24 hours, *a* 2·9732, *b* 0·3211, ratio 9·2. T. M.

Pepsin in Normal and Pathological Urine. By E. STADELMANN (*Zeit. Biol.*, **25**, 208—231).—A proteolytic ferment acting like pepsin in an acid medium has been found by many observers in urine. Neumeister (Abstr., 1888, 516) brought forward a proof that this is pepsin, when he showed that in Carnivora injection of primary albumoses into the circulation caused the appearance of deuteroalbumose in the urine; and deuteroalbumose when injected was similarly converted into true peptone.

In the present research, the question whether the ferment is pepsin or another ferment something like pepsin was investigated by performing experiments with the ferment outside the body on fibrin; and the results may be thus summarised:—

(1.) The ferment is true pepsin, as by its action all the products of peptic digestion are formed: protoalbumose, heteroalbumose, deuteroalbumose, and peptone. (2.) If, however, the solution contain but little ferment, the only products of digestion are acid-albumin and small quantities of the primary (proto- and hetero-) albumoses; and, indeed, these products can be obtained by the action of 0·25 per cent. hydrochloric acid without any pepsin on raw fibrin; the same strength of acid has no action on boiled fibrin; but 1 per cent. hydrochloric acid acts energetically by itself on boiled fibrin, forming even deuteroalbumose and peptone.

The influence of small quantities of various salts on tryptic digestion has been investigated by Nasse (*Pflüger's Archiv*, **11**), Heidenhain (*ibid.*, **10**), and A. Schmidt (*ibid.*, **13**). This same question is here investigated for peptic digestion. A number of specimens, each containing the same amount of artificial gastric juice and fibrin, were taken, with different amounts of various salts, and the time noted in which solution of the fibrin occurred. A concentration equal to 0·02 per cent. of various urates was found to exert inhibiting influence on the action of pepsin; much smaller percentages (0·004) of sodium sulphate, potassium sulphate, ammonium sulphate, and magnesium sulphate produced the same effect, whilst sodium chloride and sodium phosphate only exerted a similar action when present to the extent of 0·01 per cent.

The urine of various patients was investigated as follows: The urine was divided into three parts: (1) was diluted with 0·25 per cent. hydrochloric acid in the proportion of 1 of urine to 3 of dilute acid; (2) fresh, raw fibrin was added to extract the ferment, the fibrin was then washed and digested in 0·25 per cent. hydrochloric acid; (3) was the control specimen; it was treated as in (1), but was also boiled, fibrin being then added to each. Trypsin was sought for but never found. In fever patients, pepsin seems never absent from the urine; this includes typhoid fever, in which some have failed to find the ferment. Also in severe cases of stomach disease, including cancer, pepsin was often found. No diagnostic value can therefore be attached to the presence or absence of pepsin in the urine in cases of disease. W. D. H.

Formation of Volatile Fatty Acids in the Ammoniacal Fermentation of Urine. By E. SALKOWSKI (*Zeit. physiol. Chem.*, **13**, 264—274).—The peculiar smell of ammoniacal urine is chiefly due to the formation of volatile fatty acids.

A quantity of normal urine was divided into two parts, one part was distilled with strong sulphuric acid, the other was allowed to undergo the ammoniacal change, and then similarly distilled. The distillates were then titrated with $\frac{1}{4}$ normal sodium hydroxide solution. As a mean of eight analyses, the distillate of 300 c.c. of fresh urine contained acid equivalent to 2 c.c. of the alkaline solution, and of the stale urine, acid equivalent to 12·2 c.c. of the same solution; that is, it has increased more than sixfold. Traces of hydrochloric acid were found in both distillates, but this error is probably a constant one.

Reckoning 1500 c.c. as an average day's urine, the volatile acid per diem would be equivalent to 0·15 gram of acetic acid (a number probably a little too high), this is increased to 0·915 gram on the occurrence of putrefactive changes. In different specimens, the stronger the alkalinity of the urine the greater the amount of volatile acids obtained.

This acidity is not due to carbonic anhydride obtained by decomposition of ammonium carbonate; the ammonium carbonate in some experiments being first removed by barium hydroxide; and fresh urine mixed with ammonium carbonate gives the same amount of acidity in the distillate as a similar specimen to which ammonium carbonate was not added. The acids present appear to be acetic, propionic, and butyric. Recent researches seem to have established the fact that normal urine contains carbohydrates, and by means of the furfuraldehyde colour reaction with α-naphthol (Udránszky) these can be tested for. This reaction is, however, very weak in stale urine, hence the conclusion is drawn that the fatty acids are formed from the carbohydrates during the ammoniacal fermentation. Uric acid is found only in traces in putrid urine: ceratinine is, however, fairly abundant. Acetone is apparently unaltered by the ammoniacal fermentation; phenol and cresol are increased in quantity; the power of reducing copper oxide or silver oxide in alkaline solutions is fairly strong in putrid urine. W. D. H.

Evolution of Hydrogen Sulphide in Urine and the Behaviour of Sulphur in the Organism. By E. SALKOWSKI (*Chem. Centr.*, 1888, 1471, from *Berlin klin. Wochensch.*, **25**, 722—726).—The author considers that the evolution of hydrogen sulphide from urine is to be traced to the action of bacteria on the neutral sulphur compounds contained in the urine. It accordance with this, it was found that when nutritive solutions containing suitable thiosulphates were inoculated with urine already containing hydrogen sulphide, large quantities of hydrogen sulphide were liberated, showing the reducing power of such bacteria. Similar experiments on sulphates were attended with a like result. No trace of thiosulphates could, however, be detected in healthy urine.

Experiments made to determine the ultimate disposal of flowers of sulphur introduced into the intestinal canal showed that a part was absorbed, and of this, one part went to form sulphuric acid, whilst the remainder was separated as neutral sulphur compounds ("neutraler Schwefel"). During the hydrogen sulphide fermentation, only a part of the sulphate was reduced; how large this proportion was could not be ascertained. J. W. L.

Physiological Effect of Amyl Nitrite. By T. L. BRUNTON and T. J. BOKENHAM (*Pharm. J. Trans.* [3], **19**, 491).—The authors have found that officinal nitrite of amyl is uncertain in its action by reason of the absence or small proportion present of the active constituent, the loss being due either to its volatility or to some chemical change in the liquid. The freshly made nitrite was alone trustworthy; specimens a few days old having been found ineffectual in producing the usual physiological results. It is suggested that the freshly prepared nitrite should be put up for use in small glass capsules. The authors infer from physiological experiments, which are detailed in the paper, that the preparation is indebted for its medical efficacy less to either one or other of the two amyl nitrites than to the isobutyl nitrite which is known to be present in the ordinary "amyl nitrite." The great importance of an investigation that would determine the physiologically active ingredient, and secure its presence in determinate quantity in the officinal preparation, is pointed out. R. R.

Formation of Adipocere. By K. B. LEHMANN (*Bied. Centr.*, 1889, 66).—Horse-flesh was placed in a flask and exposed to a continuous stream of a pure river water. After seven months had elapsed, it was found that the fatty acids had increased 100 per cent. as compared with another similar piece of flesh which had been preserved in alcohol.
E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

Influence exerted by Salicylic Acid on the Proportions of Glycerol and Alcohol formed in Wines. By L. WEIGERT (*Chem. Centr.*, 1885, 1511, from *Mitt. Chem.-physiol., Versuchs-Stat., Klosterneuburg bei Wien*, **5**, 54—58).—Experiments conducted by the author on the influence exerted by salicylic acid on the rate of fermentation of must, show that the addition of 20—40 grams of the former per hectolitre of the latter retards, but does not ultimately prevent, the fermentative process. The influence exerted is not always the same; in two cases, in which 20 grams of salicylic acid per hectolitre was employed, 10·46 volume per cent. of alcohol and 4·8 per cent. of extract, and 8·37 volume per cent. of alcohol and 2·89 per cent. of extract were obtained. In another comparative experiment, in which 40 grams of salicylic acid per hectolitre was employed, 6·16 volume per cent. of alcohol and 11·5 per cent. of extract and 7·64 volume per cent. of alcohol and 3·6 per cent. of extract were obtained. The proportion of glycerol formed is not altered by the addition of salicylic acid.
J. W. L.

Asparagine and Tyrosine in Dahlia Bulbs. By H. LEITGEB (*Chem. Centr.*, 1888, 1397, from *Mit. bot. Inst. Graz*, **1**, 215—236).—The author has found that the presence of considerable quantities of these substances may be overlooked when extracted from the bulbs with alcohol, owing to the presence of a viscid liquid substance which prevents them from crystallising. J. W. L.

Juice of Bassia Latifolia. By E. HECKEL and F. SCHLAGDENHAUFFEN (*Compt. rend.*, **108**, 103—105).—The dried juice of *Bassia latifolia* forms a rosy-white, somewhat hard and compact mass, resembling gutta-percha, but becoming soft and even sticky when kneaded. At 105°, it loses 60 per cent. of water. In order to remove woody fibre, &c., it is treated with warm water acidified with sulphuric acid, well squeezed, and dried on a water-bath. It is pale brown, hardens after some days, and becomes covered with a white efflorescence readily soluble in chloroform, carbon bisulphide, and hot alcohol, but almost insoluble in cold alcohol. From hot solutions, it separates in a gummy mass, which is easily powdered when dry. Sulphuric acid colours the substance yellow and then brown, and the colour is not altered by chloroform, but if ferric chloride is added to the mixture the upper layer becomes rose-coloured and afterwards blue; this reaction is not due to the presence of cholesterin. Concentrated nitric acid produces no picric acid, and it is not affected by hydrochloric acid or by fused potash. When heated, it decomposes without forming any crystals. The substance has the composition $C_8H_{12}O$. The portion insoluble in alcohol or acetone has the consistency of gutta-percha, but is much more adhesive and hardens more easily. It is not likely to replace gutta-percha, but a mixture of equal parts of the two substances may be used for galvano-plastic moulds, and softens very readily in warm water. The ash of the substance contains a small quantity of sodium chloride, calcium phosphate, and a large proportion of calcium sulphate. C. H. B.

Analyses of Fruits from the Southern States, with reference to their Food Values. By C. L. PARSONS (*Amer. Chem. J.*, **10**, 487—488).—König, in his summary of fruit analyses, has but one analysis of oranges. The examination of eight varieties of Florida oranges, as well as pomegranates and persimmons, is now described, and the results given in a table. The flavour and general edibility of Florida oranges varies nearly with the percentage of cane-sugar; this varies from 0·84 and 0·97 in bitter-sweet and sour oranges, to 8·07 in the Mandarin orange. H. B.

Leguminosæ in Acid Soils. By P. DE MONDESIR (*Compt. rend.*, **108**, 62—64).—It is generally supposed that the presence of calcium carbonate in a soil is essential to the proper growth of leguminosæ which can be used as fodder. The author finds, however, that lupins, clover, and other leguminosæ will grow luxuriantly in the acid soils in the department of La Manche, provided that the soils are mixed with phosphates or with phosphates and potassium chloride. No improvement was obtained by mixing the soil with lime without phosphates. The superphosphates, which are themselves acid, act even more beneficially than the normal phosphates. It follows from these results that calcium carbonate is not essential, but in presence of phosphates and potassium salts, leguminosæ can obtain sufficient calcium from the compounds of the latter with the humous substances which are present in the soil. C. H. B.

Phosphates and Cereals. By J. RAULIN (*Compt. rend.*, **108**, 64—66).—The author has repeated the experiments made in 1877 (Abstract, 1888, 85). 200 kilos. of phosphoric anhydride per hectare being added in the form of natural phosphates the first year, and 40 kilos. per hectare in the following year. Similar plots were treated with only 40 kilos. of phosphoric anhydride per hectare in the form of soluble or precipitated phosphates, the same amount being added each year. The results show that fossil phosphates can be used with the same success as precipitated or soluble phosphates, provided that in the first year the fossil phosphates are added in five or six times the usual quantity. The experiments were made with maize and wheat, and the results were most strongly marked in the case of maize.

C. H. B.

Analysis of a Soil from Washington Territory. By E. A. SCHNEIDER (*Amer. J. Sci.*, **36**, 236—247).—The author has examined a soil of the following composition from Washington Territory, which is derived from a rock of the composition given below:—

	Insoluble in HCl.	Insoluble in Na_2CO_3.	SiO_2 soluble in Na_2CO_3.	Organic matter.
Rock	75·41	63·84	1·57	—
Soil..........	71·42	63·69	7·73	3·52

	SiO_2.	P_2O_5.	SO_3.	H_2O.	K_2O.	Na_2O.	CaO.
Rock	50·85	0·76	0·05	0·34	1·13	2·37	9·33
Soil.......	58·16	0·43	0·07	1·77	1·68	2·56	4·57

	MgO.	FeO.	Fe_2O_3.	Al_2O_3.
Rock	5·57	7·11	10·03	12·54
Soil	1·99	—	10·59	15·03

The results, except the first three, in each case are by fusion of the rock and soil. By sifting, the soil was divided into particles above 2 mm. cube, between 2 mm. and 0·6 mm., and below 0·6 mm. the latter constituting the bulk of the sample; this was mechanically analysed by Hilgard's method and 14·46 per cent. of brownish-yellow clay was obtained; 17·38 per cent. of brick-red sediment with hydraulic value less than 0·25 mm.; 51·17 per cent. of light chocolate stuff between 0·25 and 8 mm. h.v., and 16·86 per cent. of greyish-black sediment resembling the mother rock, with hydraulic value 8 to 64 mm. Each of these and the siftings above 2 mm. were analysed, both by fusion and by extraction with hydrochloric acid; the results are tabulated in the original. The coarsest particles approach nearest to the mother rock in composition, the lime and phosphoric acid are lowest in the clay, but when the clayey water was evaporated down instead of separating in the ordinary way, the percentage of these constituents in the residue was CaO 2·60, P_2O_5 0·65, as compared with CaO 0·41 and P_2O_5 0·11 in clay separated in the ordinary way. There is a great difference between the amount of the various constituents dissolved by hot or by cold hydrochloric acid, and the variation is different for each constituent and in different soils. The author points out that plants probably derive their nutrition from the finest particles of the soil, and, there is good reason to suppose, by the help of carbonic and feeble organic acids; therefore he does not consider chemical analysis as suitable for deciding as to the fertility of a soil, because although the larger proportion of the valuable constituents may be so locked up in the larger particles as to be inaccessible to the plants, yet they would succumb to the attacks of boiling hydrochloric acid, and then from the analytical results, these imprisoned constituents would be erroneously registered as useful to vegetation. D. A. L.

Algerian Soils. By A. LADUREAU (*Compt. rend.*, **107**, 1154—1155).—The soil of Algeria is generally deficient in phosphates. In the department of Algiers, the quantity of phosphoric anhydride per kilo. varied from 0·30 to 1·97 grams, the mean being 0·76; in the department of Oran, the limits are 0·23 and 1·37, the mean being 0·54; in the department of Constantine, the mean is 0·69, and the limits 0·30 and 1·25. The general mean is 0·68. C. H. B.

Action of Ferrous Sulphate in Various Soils. By P. M. DELACHARBONNY and L. DESTREMX (*Bied. Centr.*, 1889, 9—14).—Wheat was sown on soils containing quantities of iron varying from 1·740 to 4·321 per cent.; it was observed that the sulphate was productive of increased yield only when the iron of the soil was present in small quantities, the increase ceasing when the percentage of ferric oxide reached 3 per cent., and was detrimental when the percentage was 4 per cent. In a second experiment, when potatoes were the crops (the land being deficient in lime, lime was added in the form of sulphate and carbonate) the same results as to yield were noted. The same results were likewise observed when lucerne and hay were grown. Ferrous oxide appears to be a good manure for pastures in which much moss is present, and may be applied at the rate of 300 kilos. per hectare, or more if necessary; it may be applied dry, or dissolved in water in the ratio of 5 kilos. per hectolitre, and in the month of March.

E. W. P.

Comparative Manurial Value of the Nitrogen in Sodium Nitrate and Ammonium Sulphate. By BAESSLER (*Bied. Centr.*, 1889, 14—18).—Potatoes being the crop experimented on, and the soil sandy, it was found that ammonium sulphate, even when in combination with sodium nitrate, did not produce an increased yield commensurate with the extra expense; on the other hand the sodium nitrate was very effective. In 1888, oats were grown on humous sand, which had previously received 40 kilos. of phosphoric acid per hectare, after which sodium nitrate and ammonium sulphate were added; in this case, both manures produced a like increase of the grain, but the nitrate brought a greater yield of straw. The good action of the sulphate is ascribed to the wet weather. E. W. P.

Bat's Guano from Cuba. By A. PETERMANN (*Chem. Centr.*, 1888, 1438, from *Bull. Stat. agr. Gembloux*, 1888, **42**, 1—5).—The analysis of two specimens gave the following percentage results:—

	P_2O_5.	N.	K_2O.
I.	6·2	8·0	1·0
II.	11·8	2·0	1·7

A third specimen, also from Cuba, consisted almost entirely of potassium sulphate. The magnitude of these deposits is not known to the author. J. W. L.

Analytical Chemistry.

Draught Arrangement for Water-baths. By C. WINKLER (*Ber.*, **21**, 3563—3567).—The arrangements for keeping water-baths supplied with water and the draught cupboards in which they are placed are described with sketches.

Volumetric Estimation of Sulphur by means of Barium Chloride. By C. and J. J. BERINGER (*Chem. News*, **59**, 41—42).—The authors have made numerous experiments with solutions of 500 c.c. each, containing 10 c.c. of acetic acid and 10 grams of sodium acetate, in some cases with the addition of varying quantities of sulphuric acid, whilst in other cases 20 c.c. of sulphuric acid and varying quantities of different salts were added. In most cases, the sulphuric acid could be readily titrated with barium chloride, even in the presence of 5 grams of sodium, ammonium, zinc, ferric, or copper chloride, or of 5 grams of potassium nitrate or nitrite, or of 1 gram of calcium chloride, but with ferrous chloride the results were low, and with sodium phosphate or arsenate high, therefore, if present, the former must be oxidised, and the latter precipitated by means of ferric chloride. For estimating sulphur, the mineral or other substance is dissolved in water; if necessary being first oxidised with nitric acid, or by fusion with 5 grams of nitre, or with fusion mixture. The solution is mixed with acetic acid and sodium acetate, so that no free mineral acid is left in the solution, which is then made up to half a litre, and while steadily boiling is titrated with barium chloride, until a test quantity just shows a precipitate with sulphuric acid. The method gives good results. As much as 100 c.c. of acetic acid and 50 grams of sodium acetate have been employed in experimental solutions without impairing the results. Titrations in the cold are altogether unsatisfactory. D. A. L.

Estimation of Hydrogen Sulphide. By L. L. DE KONINCK (*Zeit. angew. Chem.*, 1888, 311).—The author published, in 1870, a method for the determination of hydrogen sulphide, which consisted in absorbing it by a solution of silver nitrate and oxidising the washed silver sulphide by bromine-water, when, after filtering from silver bromide the sulphuric acid was obtained in a solution free from non-volatile substances. He now replaces the silver nitrate by a solution of mercuric cyanide mixed with ammonium chloride. Such a solution gives, with hydrogen sulphide, a flocculent precipitate easily collected and washed. This dissolves readily and completely when warmed with bromine-water. The mercuric bromide produced being soluble as well as volatile, the advantage of the former method is attained without filtration. The single test determination reported, made on a measured volume of pure hydrogen sulphide, gave a very satisfactory result. M. J. S.

Estimation of Nitrogen by Kjeldahl's Method. By L. L'Hote (*Compt. rend*, **108**, 59—62).—The results obtained by Kjeldahl's method were compared with those obtained by means of soda-lime.

	Kjeldahl.	Soda-lime.
Caseïn	13·32	9·24—9·56
Dried blood	11·83	11·47
Powdered horn	13·66	13·46
Wheat flour (1)	2·22	1·84
" (2)	2·38	2·05
Vegetable soil (St. Pierre)	0·0870	0·0730
" " (Sèvres)	0·3720	0·3180

The substance was heated with concentrated sulphuric acid, mercury, and mercuric oxide or anhydrous cupric sulphate, and was then mixed with sodium hydroxide and sulphide. C. H. B.

Note by Abstractor.—No mention is made of the addition of potassium permanganate, and the omission of this part of the process would account for the low results, since it is known that the addition is essential in the case of substances which are not readily oxidised. C. H. B.

A Source of Error in the Estimation of Nitrates in Soils. By M. Giunti (*Chem. Centr.*, 1888, 1496, from *Staz. sperim. agrar. ital.*, **15**, 5—15).—The experiments carried out by the author show that, during the time occupied in extracting the nitrates from soils prior to their determination, the quantity of nitrates is reduced considerably, owing to the micro-organisms; at temperatures varying between 24° and 27°, the diminution amounted to a quarter to one-half of the quantity of nitrates present per 24 hours, whilst at a temperature of 15° to 17°, it amounted to nearly as much, although at first it was less. The author has made comparative experiments with different soils, and, in addition to the ordinary method, has made comparative determinations after sterilising with chloroform. In the latter case, no diminution of the amount of nitrates occurred at the end of six days. He recommends, therefore, sterilisation of the soil before extracting the nitrates. J. W. L.

Estimation of Nitrates in Natural Waters. By L. Spiegel *Ber.*, **21**, 3568).—A claim to priority (compare *Zeitsch. f. Hygiene*, **2**, 163) as regards the use of diphenylamine for this purpose (compare Hooker, this vol., p. 312).

Calculation of Phosphoric Acid Estimations. By W. MIELCKE (*Zeit. angew. Chem.*, 1888, 288).—A table giving the percentage of phosphoric anhydride for every 2 milligrams of magnesium pyrophosphate between 0·04 and 0·32 gram, when 0·5 gram of substance is employed. M. J. S.

Direct Estimation of Phosphoric Acid as Tricalcic Phosphate. By H. TZSCHUCKE (*Zeit. angew. Chem.*, 1888, 383—385).—To the phosphate solution, there is added so much hydrochloric acid that calcium chloride produces no precipitate, then calcium chloride, and, lastly, an excess of ammonia. The mixture is immediately diluted with twice its volume of cold water, filtered at once on a rapid filter, and the precipitate washed with cold water. The excess of calcium chloride must not be large, and warming is to be avoided. Substances which already contain sufficient calcium have simply to be dissolved in hydrochloric or nitric acid, and precipitated by ammonia. If sesquioxides are present, the phosphoric acid combined with them must be determined separately. In the case of impure substances, the results are admittedly only approximate, but the facility of the determination gives it a certain value. M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By M. A. v. REIS (*Zeit. angew. Chem.*, 1888, 354—362).—The methods proposed for this purpose are already very numerous. The mode of dissolving the substance has been varied according to the views held respecting the presence and value of the iron phosphide. The author has not met with this compound in the slag, and regards its occurrence as so rare that it need not be taken into consideration. He has made comparative experiments on the following methods of effecting solution:—Klein's fusion method (Abstr., 1886, 740); Kosmann's aqua regia treatment (Abstr., 1881, 489); treatment with nitric acid (Jensch); Brunnemann's process with aqua regia and sulphuric acid (Abstr., 1887, 527); Klein's, with hydrochloric acid (Abstr., 1886, 835); the same as used by Thilo and by Kennepohl without removal of silica (Abstr., 1888, 321); Vogel's cold treatment with hydrochloric acid; Müller's, with hydrofluoric acid; Mohr's, with dilute sulphuric acid (Abstr., 1887, 864); and that of Ende and Loges with concentrated sulphuric acid (Abstr., 1887, 527). The results from all these methods agreed within 0·15 per cent., showing that the simplest of them, the treatment with hydrochloric acid without removal of silica, may be adopted when the phosphoric acid is thrown down by molybdate. Of methods of determination, the following were tested:—A, weighing as magnesium pyrophosphate after precipitation with molybdate; B, precipitation by molybdate at 90° from a solution containing 20 per cent. of ammonium nitrate, and weighing, after drying at 100—110°; C, determination as molybdenum phosphomolybdate by igniting the precipitate thrown down at about 40° (Meineke); D, Korschelt's potassium molybdate method; E, Thilo's ammonia titration method (Abstr., 1887, 526), which, for its convenience and rapidity, the author prefers to all others, where extreme accuracy is not wanted. The most suitable indicator is azolithmin. The change of colour is somewhat gradual, but the reddish-violet tint corresponding to the point of neutrality is easily recognised after practice; F, Schindler's titration with lead acetate (Abstr., 1888, 753, 757); G, determination of the ammonia in the precipitate, according to Isbert and Stutzer (Abstr., 1888, 194); K, Mallot's uranium titration method (Abstr., 1887, 1063); I, Mohr's uranium method (*loc. cit.*); L, direct precipitation by magnesia mixture, after adding citric acid (see Vogel, Abstr., 1888, 991). Following Vogel's instructions exactly, the results came out too high, the precipitate being contaminated with silica, lime, and iron. The filtration, moreover, is very tedious. The following improved process is recommended:—10 grams of the powdered slag is boiled with 50 c.c. of concentrated hydrochloric acid; 50 c.c. of concentrated sulphuric acid is then added, and the mixture heated until white fumes appear. After dilution, it is again boiled until all the iron is in solution, then cooled and made up to 504 c.c. 32 c.c. of the filtered liquid is then precipitated according to Vogel's directions. Each centigram of pyrophosphate corresponds to 1 per cent. of phosphoric acid. The whole determination requires 2½ hours. M, precipitation by molybdate in citric acid solution (Werenskjold). The reagent used is prepared by dissolving 300 grams of ammonium molybdate to 1 litre, adding half a litre of 50 per cent. citric acid solution, heating, adding half a litre of nitric acid (1·4), boiling until any traces of phosphoric acid present are precipitated, and then oxidising the reduced molybdic acid by a few c.c. of hydrogen dioxide. The reagent and the phosphate solution should be boiling when mixed, and the mixture kept for 5 or 10 minutes at 100°. The weight of the precipitate, multiplied by 0·03933, gives that of the phosphoric anhydride. N, ignition of the precipitate obtained as in B. The results are more regular than those obtained by drying at 100°. With the exception of D, G, and I, which are condemned, these methods all give fairly concordant results; L is the best for accuracy, E for rapidity. M. J. S.

Decomposition of Insoluble Silicates. By A. Johnstone (*Chem. News*, **58**, 310).—A small quantity of the silicate is placed on a layer of ammonium fluoride in a platinum crucible or on a piece of platinum foil and heated before the blowpipe; when most of the fumes have passed away, a little more fluoride is pressed into the mass and the whole again heated. After repeating this operation, usually five or six times, the silicates are sufficiently decomposed for the identification of the bases. Felspars, mica, garnet, zircon, &c., have been successfully treated by this method. D. A. L.

Estimation of Carbonic Anhydride in the Air for Hygienic Purposes. By G. Lunge and A. Zeckendorf (*Zeit. angew. Chem.*, 1888, 395—399).—The authors adopt the principle of Angus Smith's minimetric method, but instead of observing the first appearance of turbidity in a solution of an alkaline earth, they employ a dilute standard solution of sodium carbonate coloured with phenolphthaleïn, and ascertain the volume of air required to produce decoloration by the conversion of the normal into the hydrogen carbonate. They recommend an india-rubber hand-pump delivering 70 c.c. at each compression and furnished with valves. This delivers the air into a bottle of 110 c.c. capacity in which it is shaken with 10 c.c. of the soda solution, prepared by diluting a decinormal solution (to which 1 gram of phenolphthaleïn per litre has been added) 50-fold with boiled water. With these conditions, air containing 0·3 per cent. of carbonic anhydride requires two fillings of the pump, whilst 0·03 per cent. requires 48 fillings. These, and the intermediate values, were ascertained by empirical experiment, and are not applicable to apparatus of other dimensions. M. J. S.

Electrolytic Detection of Mercury. By C. H. Wolff (*Zeit. angew. Chem.*, 1888, 294—296).—The solution to be tested is passed slowly through a vertical tube containing the electrodes. The positive electrode is a spiral of stout platinum wire lying close to the walls of the tube. The negative electrode is a spiral of steel pianoforte wire, which has been first coated with copper and then silvered. If the solution contains organic matter, this is to be destroyed by hydrochloric acid and potassium chlorate. It is then acidified with 3 or 4 per cent. of sulphuric acid and passed three times through the tube at the rate of 12 or 15 drops per minute. The steel spiral is then removed, dried by dipping in alcohol and ether, and sealed up in an elongated glass bulb with drawn-out neck. After heating so as to drive the volatilised mercury into the narrow neck, the lower end of the bulb is cut off, the spiral removed, and a crystal of iodine introduced. By careful heating, the vapour of the iodine is passed over the mercury and converts it into iodide. As little as 0·01 milligram of mercury in 100 c.c. can be thus detected. If the quantity is somewhat larger, the portion of the tube containing the sublimate may be introduced into a short, wide test-tube, bedded in sand in a crucible, and be sublimed on a microscopic cover-glass. M. J. S.

Analysis of the Raw Materials and Products of the Iron Industry. By C. Meineke (*Zeit. angew. Chem.*, 1888, 252—261; compare p. 310).—*Precipitation by Ammonia.*—This is chiefly of service for the separation of the iron-group from calcium and magnesium. Blum (Abstr., 1888, 324) has called attention to a possible error arising from the dissociation of ammonium chloride on boiling, but the author shows by numerous test analyses of solutions of known composition, as well as by comparison with the carbonate and acetate methods of separation, that boiling for only a short time invariably leaves some calcium and generally magnesium in the iron precipitate. Moreover, he does not find alumina redissolved even when the boiling is continued until the smell of ammonia is no longer perceptible. An attempt was made to determine calcium by adding to the acid solution a known excess of oxalic acid, then precipitating by ammonia and titrating the excess with permanganate; but more oxalic acid passes into the precipitate than corresponds with the calcium present, in consequence, seemingly, of the formation of a double oxalate.

Neither Bloxam's phosphate method, nor that depending on the precipitation of the iron by barium carbonate, effects a complete separation of the manganese. Mercuric oxide separates iron and manganese imperfectly, but it can be used with great convenience for the determination of the alkalis in silicates decomposable by hydrochloric acid (such as blast-furnace slags). After the evaporation to render silica insoluble, the unfiltered hydrochloric acid solution is mixed with excess of mercuric oxide, and is evaporated to dryness and ignited gently. The aqueous extract will then contain nothing but the alkalis with a little calcium. The latter is separated by adding a few drops of ammonium oxalate, and the smallness of the amount of ammonium salts in the filtrate renders the treatment of the alkalis extremely easy. Alumina when present as sulphate or fluoride is not precipitated by mercuric oxide.

Precipitation by Zinc Oxide.—The sesquioxides can be completely separated from manganese, nickel, and cobalt by zinc oxide. The process of Mathesius consists in oxidising with bromine, evaporating to dryness, taking up with hydrochloric acid, nearly neutralising with ammonia, and precipitating with zinc oxide. After partial filtration, the manganese is precipitated by Wolff's method with bromine and a current of air containing ammonia. The precipitate contains zinc as well as other impurities to the extent of several per cent. After re-solution and reprecipitation, zinc is no longer present, but the presence of other oxides raises the result beyond admissible limits.

Precipitation by Nitroso-β-naphthol.—This method proves very advantageous for the separation of iron, copper, and cobalt from manganese. The iron precipitate is free from manganese. Traces of iron, however, pass into the filtrate and are found in the manganese precipitate, which is further liable to be contaminated with silica and nickel. A great advantage of this method is that it accurately separates iron and alumina, the latter not being precipitated by nitroso-β-naphthol. It can be thrown down by ammonia from the filtrate as usual, and if but little manganese is present, the copious addition of ammonium chloride prevents it from precipitating with the alumina. The determination of calcium and magnesium is not interfered with by the nitroso-β-naphthol. Phosphoric acid will be entirely precipitated with the iron if acetic acid is the only free acid. M. J. S.

Volumetric Estimation of Cobalt in presence of Manganese, Nickel, &c. By N. McCulloch (*Chem. News*, **59**, 51—52).—Cobalt in the presence of cyanides reduces chromic acid in accordance with the equation $6Co(CN)_2 + 24KCN + 2CrO_3 + 3H_2O = 3K_6Co_2(CN)_{12} + Cr_2O_3 + 6KHO$, and the resulting potassium cobalticyanide is a stable compound of constant composition. On this basis, the author has devised the following method for the estimation of cobalt in the presence of nickel, manganese, lead, arsenic, or phosphorus; copper must be absent and iron is best eliminated. Standard solutions of dichromate and potassium cyanide in suitable proportions, and a few drops of ammonia, are boiled in a flask fitted with a double-bored cork carrying a thistle funnel dipping into the liquid and a tube for the escape of steam; the hot solution to be examined is then poured down the funnel, and the whole treated with warm, concentrated ammonium chloride solution and boiled to expel volatile cyanides. To prevent the formation of ferrous cobaltocyanide and double cyanide of iron and nickel in the subsequent treatment with ferrous salt, nickel sulphate solution is added until no further precipitate is formed, but not in great excess. The contents of the flask are poured into excess of hot standard ferrous ammonium sulphate solution, acidified with a few drops of hydrochloric acid, and titrated with dichromate in the usual way. The percentage of cobalt is calculated from the dichromate reduced in the first instance. A correction, which should be ascertained by blank experiments, must be made for the dichromate reduced by boiling with the cyanide and ammonia. The author strongly recommends the method. D. A. L.

Estimation of Chromium, Iron, and Manganese by means of Hydrogen Peroxide. By A. CARNOT (*Compt. rend.*, **107**, 997—1000 and 1150).—Chromic acid in an acid solution is reduced by hydrogen peroxide, but in alkaline solutions chromic salts are oxidised to chromates by this reagent. A dilute solution of a chromium salt is heated to 100°, mixed with a few cubic centimetres of hydrogen peroxide, then with excess of ammonia, and again heated to boiling. The solution at first becomes turbid and brown, but the colour rapidly changes to pale-yellow owing to the formation of ammonium chromate. If any chromic oxide remains unoxidised, it is allowed to subside and is redissolved in acid and again treated in the same way. After boiling to expel excess of hydrogen peroxide, the chromic acid formed may be estimated volumetrically by hydrogen peroxide (this vol., p. 311). The solution from this operation may be mixed with sodium or ammonium acetate and the chromium precipitated with sodium phosphate.

After boiling with hydrogen peroxide and ammonia, and separation of the metals precipitated by ammonia, the chromate may be reduced by hydrogen sulphide and the chromium precipitated by adding ammonia.

In the case of mixtures of chromates and chromic salts, the chromic acid is first estimated volumetrically by hydrogen peroxide, and the total chromium in the same solution is precipitated as phosphate or hydroxide. In the case of solutions containing chromium mixed with iron or aluminium, the former is oxidised to chromic acid, which is estimated by hydrogen peroxide, and in the same solution the chromium and iron or chromium and aluminium are precipitated together, the aluminium or iron being estimated by difference.

If an ammoniacal solution of a manganese salt is mixed with hydrogen peroxide and boiled, a precipitate is obtained of the composition Mn_6O_{11}, but it can only be purified from other bases by repeated re-solution and reprecipitation. The manganese in this precipitate can, however, be more readily determined volumetrically by means of standard oxalic acid, sulphuric acid, and potassium permanganate, $O_5 = Mn_6$. C. H. B.

Estimation of Titanium in Natural Silicates. By P. HOLLAND (*Chem. News*, **95**, 27—29).—In preliminary experiments, the author satisfied himself that titanium oxide does not suffer loss when it is treated with hydrofluoric acid in presence of sulphuric acid, although the loss is great when none of the latter acid is present (Riley, this Journal, 1859, 13), and that titanic oxide may be completely precipitated after fusion with potassium hydrogen sulphate. He finds the following method gives good results:— 2 grams of titaniferous rock or mineral is moistened with dilute sulphuric acid in a platinum crucible, and 5 grams of hydrofluoric acid is gradually added. The crucible is now covered and heated in an air-bath, starting at 100° but subsequently raising the temperature until the residue appears dry; concentrated hydrochloric acid is added and the crucible is again heated. Any undissolved titanic oxide is collected on a filter, ignited, fused with potassium hydrogen sulphate, dissolved, and the filtered solution added to the hydrochloric solution, which has been oxidised by a few drops of chlorine-water, and the combined solutions are made up to half a litre and divided into two portions. In one, the alumina, ferric, and titanic oxides are precipitated together by means of ammonium acetate, care being taken to remove all the alumina from the solution by further precipitation. The united precipitates are weighed, finely powdered, and fused with potassium hydrogen sulphate, quickly extracted with water at 80° containing a little sulphuric acid, made slightly alkaline with ammonia and boiled for 20 minutes. The precipitate is dried, ignited, re-fused, re-treated, then ultimately weighed as titanic oxide. In the other portion of the solution, the iron is estimated, and the amount of alumina is ascertained by difference from the weight of the combined alumina, ferric and titanic oxide precipitate. This method does not answer in the presence of phosphoric acid. Ignited titanic oxide is insoluble in hydrochloric acid, but when it is ignited in the presence of alumina it becomes almost completely soluble in that solvent; for this reason, Roussel's process for estimating titanic oxide does not answer if his directions are exactly followed; it is better to treat the precipitate of alumina, titanic acid, and sulphur (obtained by boiling the acid solution with sulphurous acid and sodium sulphate and thiosulphate) with carbon bisulphide and then with dilute sulphuric acid to dissolve the alumina. D. A. L.

Detection of Antimony in Minerals. By A. JOHNSTONE (*Chem. News*, **58**, 296—297; **59**, 15).—The mineral is heated on charcoal before the blowpipe or in an open tube in the usual way, and the white sublimate obtained is treated with a drop of ammonium sulphide; a change in colour from white to orange is a sure indication of the presence of antimony, as antimonious oxide is converted into the orange sulphide by this treatment. D. A. L.

Volumetric Estimation of Antimonic Acid. By A. JOLLES (*Zeit. angew. Chem.*, 1888, 261).—The antimony in antimonic acid can be very conveniently determined by titration with potassium manganate after reduction by sulphurous acid. The antimoniate is made strongly acid with hydrochloric acid, a concentrated solution of sodium sulphite is added, the excess of sulphurous anhydride is boiled

off, the solution is made up to a definite volume (about 0·2 gram in 100 c.c.) and is titrated by manganate in the manner described on p. 311.
M. J. S.

Tartar Emetic. By W. R. DUNSTAN and L. E. BOOLE (*Pharm. J. Trans.* [3], **19**, 385—387).—The authors point out various sources of error in the process prescribed by the British Pharmacopœia for the determination of antimony in tartar emetic. They advocate a volumetric method, depending on titration with a solution of iodine immediately after the addition of sodium hydrogen carbonate; the method is accurate. When alcohol is added to an aqueous solution of tartar emetic, that substance is precipitated in the anhydrous state.
R. R.

Decomposition and Estimation of Iodoform by Silver Nitrate. By GRESHOFF (*Rec. Trav. Chim.*, **7**, 342).—Silver nitrate acts readily on iodoform at ordinary temperatures as follows:—$CHI_3 + 3AgNO_3 + H_2O = 3AgI + 3HNO_3 + CO$. The reaction takes about an hour and a half for its completion, and the nitric acid set free can then be titrated.
H. C.

Analysis of Alcohols. By C. GIRARD and X. ROCQUES (*Compt. rend.*, **107**, 1158—1159).—When aldehyde is mixed with an alcoholic solution of metaphenylenediamine hydrochloride, the liquid becomes orange-red, and if agitated in presence of air the colour deepens, and an intense fluorescence is developed. This coloration is not affected by acetic acid, but changes to pale yellow and the fluorescence disappears on addition of ammonia. The compound formed is stable and remains in the retort when the alcohol is distilled.

200 c.c. of alcohol of 50° is mixed with 3 grams of metaphenylenediamine hydrochloride, boiled for half an hour in a flask attached to a reversed condenser, allowed to cool, and the pale yellow liquid, when agitated repeatedly, becomes dark coloured and fluorescent. 125 c.c. of the alcohol is distilled off rapidly and amyl alcohol is estimated in the distillate by Savalle's method. If the amyl alcohol is only present in small quantity the whole of it passes over with the 125 c.c.
C. H. B.

Estimation of Alcohol in Essential Oils. By H. HAGER (*Chem. Centr.*, 1888, 1512—1513, from *Pharm. Zeit.*, **33**, 650—651).—Since glycerol, containing 20 per cent. of water, mixes completely with alcohol but does not dissolve the essential oils, the following method, based on this principle, is recommended. Into a graduated tube 8—10 cm. long and 7—9 mm. wide, 1·5—3 cm. of glycerol is introduced, and after noting the volume, 2—3 c.m. of the essential oil is added and the volume again read off. After shaking and subsequent separation of the liquids, the increase in the volume of the glycerol is noted. Instead of measuring the liquids, the determination may be made gravimetrically, the essential oil being absorbed by means of blotting-paper from the surface of the glycerol layer, and the latter weighed.
J. W. L.

Estimation of Glycerol in Wine. By L. WEIGERT (*Chem. Centr.*, 1888, 1511, from *Mitt. chem.-physiol. Versuchs-Stat., Klosterneuburg bei Wien*, **5**, 59—62).—The following method is recommended:—100 c.c. of wine (sour, not sweet) is concentrated on the water-bath to 3—5 c.c., 3—5 grams of slaked lime is added, and then 50—80 c.c. of 90—96 per cent. alcohol, the mixture being then heated on the water-bath until the alcohol has boiled a few minutes. The solution is then filtered, treated a second time with 43—50 c.c. of the alcohol, and the whole brought on to the filter and washed with 50—80 c.c. of alcohol. The filtrate is concentrated on the water-bath, preferably in a 230—250 c.c. flask, to a syrup, 10—20 c.c. of absolute alcohol and 15—30 c.c. of ether added, and after the solution has cleared, the ether layer is poured off into the weighing glass. The residue is again treated with a mixture of alcohol (1 part) and ether (1½ part), and the extract added to the first. The ether and alcohol are evaporated off, and the glycerol remaining finally weighed.

In the case of sweet wines, no calcium hydroxide is employed, but in other respects the procedure is similar. The glycerol should always be tested for sugar. In judging a wine, in regard to the proportion subsisting between the glycerol and alcohol, the presence of acetic acid, or the addition of salicylic acid, whether the proportion of nitrogen varies much from the average, or whether the wine has been strongly sulphured, should always be taken into account.

J. W. L.

Safranine as a Reagent for Grape-sugar. By L. CRISMER (*Chem. Centr.*, 1888, 1510, from *Pharm. Zeit.*, **33**, 651).—If 2 to 3 c.c. of a 1 : 1000 solution of safranine is heated in a test-tube with a few drops of a solution of grape-sugar and 2 to 3 c.c. of soda, the safranine becomes reduced, and the solution is rendered colourless and opalescent, owing to the precipitation of the decolorised dye. At the surface, the colour of the dye rapidly reappears, owing to reoxidation. The author recommends this reaction for the detection of grape-sugar in solutions, such as urine, since the safranine is not reduced by uric acid, creatinine, chloral, chloroform, hydrogen peroxide, or hydroxylamine salts, all of which reduce Fehling's solution. Egg-albumin reduces safranine slowly, but completely. J. W. L.

Detection of Salicylic Acid in Beer. By G. H. HOORN (*Rec. Trav. Chim.*, **7**, 341).—The author tested various samples of beer for salicylic acid by two methods; the first being by acidifying the beer with sulphuric acid, extracting with a mixture of ether and light petroleum, and evaporating the extract; the second by distillation of the beer after acidifying with sulphuric acid. By the first, salicylic acid could not be detected, but by the second it was detected in the later, but not in the first portions of the distillate.

It has also been ascertained that the coloration produced by ferric chloride in salicylic acid solutions is due to a volatile compound, which is also formed when the beer is distilled with sulphuric acid.

H. C.

Estimation of Salicylic Acid. By L. WEIGERT (*Chem. Centr.*, 1888, 1511, from *Mitt. chem.-physiol. Versuchs-Stat., Klosterneuburg bei*

Wien, 5, 54—58).—The author recommends shaking 50 c.c. of wine with an equal volume of chloroform, after which the chloroform layer is separated and passed through a dry filter. 30 c.c. of this is treated with 10 c.c. of ferric chloride (freshly prepared solution 1 : 1000), and shaken up well. For quantitative determinations, ether should be used in place of chloroform in a Schwarz's extractor. J. W. L.

Estimation of Foreign Acids in Artificial Salicylic Acid. By E. E. EWELL and A. B. PRESCOTT (*Pharm. J. Trans.* [3], **19**, 328—330).—Salicylic acid, manufactured from ordinary phenol, necessarily contains a greater or less quantity of homologous compounds, derived from the higher phenols. In 1878, Williams proposed a method of estimating these foreign acids, based on the less solubility of calcium salicylate. This method the authors find untrustworthy, at least on the data known at present. They give details of two new processes; one being the determination of the saturating power of the acid, in which 1 gram is titrated with centinormal alkali and phenolphthaleïn as indicator, and thus 1·8 per cent. of the other acids (calculated as hydroxytoluic acid) may be detected; the other, a plan by distilling with lime, by which salicylic acid and its homologues are converted into phenols, the amount of the respective phenols being estimated by known methods. R. R.

Estimation of Citric and Tartaric Acids when Mixed. By J. S. WARD (*Pharm. J. Trans.* [3], **19**, 380).—The author finds that quantitative determinations of mixtures of citric and tartaric acids give too low results in each case. He adopted certain modifications in the analytical process, obtaining results which, although constant, were still too low; whence he infers that calcium tartrate, in the presence of a citrate, is not completely precipitated in 12 hours, and that calcium citrate is slightly soluble in boiling water. R. R.

Tests for Tannic and Gallic Acids. By S. G. RAWSON (*Chem. News*, **59**, 52—53).—When ammonium chloride and ammonia are added to solutions of tannic acid, a white precipitate is formed which rapidly becomes red. In solutions containing 1 part of tannic acid in 5,000 of water, the precipitation is slow, and it is best to drop in the ammonium chloride and ammonia so as to form a layer on the top, then at the point of contact a distinct white line appears, even in solutions containing 1 in 20,000, whilst by holding against a black surface 1 in 50,000 may be detected. When solutions of gallic acid are treated in a similar manner, no precipitation occurs, but the liquid becomes red in strong solutions, and with dilute solutions a greenish-coloured ring forms, even when the dilution is 1 in 100,000. A red coloration is produced in solutions of either of these acids by chlorine-water and ammonia, and by potassium ferricyanide and ammonia. With the latter reagents a 1 in 10,000 solution of tannic acid becomes distinctly red, and the redness produced in a 1 in 30,000 solution is seen by looking down the test through the column of liquid, whilst by comparing with a blank, a yellowish-brown coloration may be detected in a 1 in 100,000 solution. D. A. L.

Detection of Iron in Oil. By B. EMDE (*Zeit. angew. Chem.*, 1888, 362—363).—In dyeing with alizarin on alumina mordants, the presence of traces of iron is highly injurious. To detect it in "Turkey-red oil," the oil is shaken in a cylinder with dilute sulphuric acid containing a little potassium ferrocyanide. After adding ether, it is again shaken. The whole of the iron present in the oil will then appear as a blue layer between the aqueous and ethereal liquids.

M. J. S.

The Reichert-Meissl-Wollny Method of Analysis as applied to Italian and Mixed Butters. By C. BESANA (*Bied. Centr.*, 1889, 61—65).—The analyses made, according to the above process, of a large number of Italian butters, showed that the melting point varied from 33—37·7° (one case 40·5°), and that the quantity of decinormal alkali necessary for saponification varied from 30·19 c.c. to 21·8 c.c., but that for the greater majority of samples 30 c.c. to 28 c.c. was sufficient, the remaining samples being too unusual to be taken into consideration. Besana, therefore, concludes that 28·8 c.c. may be taken as a fairly accurate factor in all necessary calculations when dealing with pure butter: further various samples of artificial butter (margarine, &c.) were examined, and 0·3 c c. is taken to be their equivalent of decinormal alkali.

To estimate the percentage of margarine, added to genuine butter in a sample of mixed butter, the following formulæ are employed:—

$$100 = b + m \text{ and } t = \frac{bt'}{100} + \frac{mt''}{100},$$

from which follows—

$$b = \frac{100(t - t'')}{t' = t''},$$

where b = percentage of pure butter; m = percentage of added fat: t = c.c. of decinormal alkali; as shown by titration of sample; t' = c.c. of decinormal alkali required for pure butter (*i.e.*, 28·8), and t'' = c.c. of decinormal alkali required for added fat (*i.e.*, 0·3). The author adds that for t', the figures 21·8, 30 2, and 27 may be employed according to opinion, in which case the maximum and minimum quantities of admixture will be obtained.

E. W. P.

Estimation of Free Caustic Alkali in Soap. By J. A. WILSON (*Chem. News*, **59**, 40).—Soap made by the cold process may contain both free alkali and free fat, consequently when dissolved in alcohol to titrate the free alkali, the latter immediately saponifies the free glycerides and vitiates the results. For this reason, the author prefers to titrate the total alkali with normal acid and methyl-orange, and to estimate in another portion the alkali required by the fatty acids of the soap. Silicates, carbonates, or borates interfere with the results, but can be easily estimated by other means.

D. A. L.

Detection of "Saccharin." By S. C. HOOKER (*Ber.*, **21**, 3395).—The reaction described by Börnstein (Abstr., 1888, 760) for the detection of saccharin cannot be depended on, as the result seems to be the same when resorcinol alone is heated with concentrated sulphuric acid.

F. S. K.

Detection of "Saccharin." By E. Börnstein (*Ber.*, **21**, 3396). The author points out that although many organic compounds can be made to yield a fluorescent solution by suitable treatment with resorcinol and sulphuric acid, yet this reaction can be employed for the detection of "saccharin," because extremely small quantities of this substance are sufficient to give a distinct reaction (compare Hooker, preceding Abstract). In testing for "saccharin" in foods, 0·005 gram of the dry residue is treated with twice its weight of resorcinol and 2 to 3 drops of concentrated sulphuric acid; if "saccharin" is present, a distinctly fluorescent solution is obtained, whereas with resorcinol alone several decigrams must be employed before the fluorescence can be observed. The green coloration which appears at the moment when the solution is made alkaline is only shown in the case of two substances besides "saccharin," namely, phthalic anhydride and phthalimide.

F. S. K.

Estimation of the Alkalinity of the Blood. By J. B. Haycraft and R. T. Williamson (*Proc. Roy. Soc. Edin.*, **127**, 396—399).—Zuntz's method (*Centr. med. Wiss.*, **51**, 1867) is the only one whereby the alkalinity of blood may be estimated quantitatively, but it is unfitted for clinical purposes, as a large amount of blood is required. The authors, requiring a method necessitating only a very small quantity of blood, experimented with many indicators, but none were found to be so effective as litmus. They prepared a series of red litmus-papers (acidified with a small quantity of oxalic acid) and glazed them by dipping into liquid paraffin oil. A single drop of blood produces a neutralising effect after a short time, as the plasma does not percolate through the glaze rapidly. After moistening with the blood, the paper is washed in distilled water and then pressed between folds of blotting-paper. The amount of alkali which will turn the red paper blue being previously known, the alkalinity of the blood can therefore be easily ascertained. The authors, however, are of opinion that, because of the difficulty of percolation above referred to, the alkalinity will not be quite identical with the amount of alkali, but as this error is uniform the usefulness of the series of litmus-papers will not be impaired for physiological purposes.

E. W. P.

Furfuraldehyde Reactions. By L. v. Udránszky (*Zeit. physiol. Chem.*, **13**, 248—263).—This has been the subject of two previous communications by the author (Abstr., 1888, 863 and 878). It has been already noted that commercial amyl alcohol cannot be used in certain researches, especially for the separation of pigments in acid liquids, as on the addition of acid it undergoes a partial decomposition resulting in the formation of a brown deposit. This is because it contains furfuraldehyde. Attempts to obtain the alcohol free from that impurity by means of animal charcoal were unsuccessful; it was, however, obtained from potassium amyl sulphate. This was dissolved in warm alcohol, and a large excess of ether added; from this solution crystals of the salt crystallised out, and were purified from all but traces of furfuraldehyde by repeated recrystallisation. The salt was then saponified by sodium hydroxide, decomposed by 10 per cent. sulphuric acid, and heated on the water-bath for five hours; the alcohol was then obtained by distillation. The properties of the alcohol so obtained are described. Quantitative estimations of the amount of furfuraldehyde in the commercial preparations of the alcohol were also made: from 0·028 to 0·074 of the coloured product were obtained. The pure amyl alcohol is very useful as a means of separating pigments, and for extracting small quantities of alkaloïds in medico-legal investigations. The colour reactions, including spectroscopic appearances of the furfuraldehyde in amyl alcohol, may be used for the detection of the latter substance in spirituous liquors.

W. D. H.

Volumetric Determination of Uric Acid. By A. M. GOSSAGE (*Proc. Roy. Soc.*, **44**, 284—285).—Haycraft's method, in which uric acid is precipitated with silver nitrate in the presence of sodium carbonate and ammonia, and the precipitate treated with ammonium thiocyanate, is compared with that of Salkowski, in which the excess of silver nitrate is determined, phosphates being previously removed with magnesia mixture. Haycraft's results are always higher than Salkowski's, as the former assumed that the precipitated urate contains one atom of silver in the molecule, whereas the proportion of silver is always larger. If Haycraft's results are divided by 2, they agree in some cases with those of Salkowski, in others they are lower.

H. K. T.

Estimation of Proteïds with Special Reference to Milk. By J. SEBELIEN (*Zeit. physiol. Chem.*, **13**, 135—180).—Milk contains three proteïds, caseïn, lactalbumin, and traces of lactoglobulin. In order to test the method adopted for the quantitative estimation of the total proteïds and of the individual proteïds, a number of preliminary experiments were made with solutions of (1) pure caseïn containing small quantities of calcium chloride and sodium phosphate, (2) lactalbumin, and (3) egg albumin. Ritthausen's copper sulphate method of precipitating total proteïds was first investigated in the following way: the total nitrogen in the proteïd solution, in the precipitate, and in the liquid from which the precipitate had been filtered off, was estimated by Kjeldahl's process. The two first named had practically the same amount of nitrogen in them, whilst the filtrate was free from nitrogen. Lead acetate was similarly tested; some proteïd was left in solution, and the nitrogen in the precipitate plus that in the filtrate gave too high a result. Tannic acid was found to precipitate all proteïds completely; the precipitate must, however, not be washed with hot water or with spirit, as it is partially soluble in both those reagents. Albumoses are only incompletely precipitated by tannic acid, and peptone is soluble in excess of the reagent. The properties of phosphomolybdic acid are much the same, except that it causes a more complete precipitation of both albumoses and peptone.

The question whether albumoses and peptone occur in milk was then investigated. Saturation with ammonium sulphate completely precipitates all proteïds but peptone, which if present, may be identified in the filtrate by the biuret reaction (Kühne), or better still by the precipitate it gives with tannic acid. Peptone is, however, absent in milk, and also in colostrum, and in whey; the whey-proteïd of Hammarsten is thus not of the nature of peptone. It is, however, present in kephir, and in "long-milk" (a preparation made from milk in Upper Scandinavia). Other portions of milk were precipitated with tannic acid, and the filtrate was found to contain only such small quantities of nitrogen as would be accounted for by the urea, hypoxanthine, and other non-proteïd constituents; albumoses are absent therefore.

The method of estimating the total nitrogen in the precipitate produced by tannic acid, and multiplying this by 6·37 to obtain the total proteïd, is recommended as the most accurate method in quantitative investigations of proteïds, and is stated to produce less error than the more usual methods involving the washing, drying, weighing, and incineration of proteïd precipitates.

In order to estimate the caseïn and lactalbumin separately, rennet and various salts added to saturation have been recommended; these were all tested, and magnesium sulphate was found to be the best; it precipitates all the caseïn and the trace of lactoglobulin which is seemingly disregarded, and leaves all the albumin in solution. Sodium chloride was also found to precipitate all the caseïn. The albumin has been estimated by others, by weighing the precipitate produced by boiling after the separation of the caseïn. But boiling was found to be a very incomplete method of precipitating it; much nitrogen occurring in the filtrate after its removal. It is suggested that boiling lactalbumin and other proteïds split them (as Hammarsten found with fibrinogen) into an insoluble proteïd which is precipitated, and a soluble one which is left in the filtrate. It was found that solutions of pure caseïn when heated do not coagulate, but become opalescent, becoming clear again, however, on cooling. With regard to colostrum, many contradictory statements are quoted as to the relative amount of caseïn and albumin. By the present method it is found that the amount of these two proteïds is very variable; that the quantity of globulin is very considerable, and that the non-proteïd nitrogenous constituents are more abundant than in milk.

The following method was adopted in the analysis:—(1.) Total nitrogen first estimated in the colostrum. (2.) Proteïd nitrogen estimated in the tannic acid precipitate. (3.) Nitrogen in the precipitate produced by saturation with magnesium sulphate (caseïn + globulin). (4.) Caseïn-nitrogen estimated in the precipitate produced by adding acetic acid to milk. (Approximate.) (5.) Globulin nitrogen; two estimations: maximal, obtained by the difference of (3) and (4); minimal, estimated in the precipitate produced by magnesium sulphate after separating the caseïn by saturating with sodium chloride. (6.) Albumin-nitrogen, estimated in the precipitate produced by adding tannic acid to the filtrate after the separation of the proteïds, precipitated by magnesium sulphate saturation. (7.) Non-proteïd nitrogen is the difference between (1) and (2).

The following table gives the results in the analysis of five specimens of colostrum:—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1...	1·232	1·025	0·887	—	0 100	0·138	0·207
2...	2·506	2·269	2·02	0·56	0·248 1·46	0·25	0·237
3...	2·566	2·461	2·147	0·534	1·604 1·613	0·314	0·086
4...	2·222	2·086	1·903	0·718	0·3 1·185	0·183	0·076
5...	1·10	—	0·716	0·55	0·081 0·166	—	—

W. D. H.

Estimation of Albumin in Urine. By A. Christensen (*Lancet*, 1, 1889, 189, from *Virchow's Archiv*, **115**, 128—143).—This new method is considered more accurate than Esbach's. The latter plan consists merely in the complete precipitation of the albumin by picric acid, and the use of a tube so graduated that the depth of the deposit at the end of 24 hours indicates so many grams of albumin per litre of urine. This was found to be variable in its results when compared with those of coagulation by heat and nitric acid, for very slight changes of temperature influence the extent to which the precipitated albumin will "settle." The new method proposed consists in the use of tannic acid as the precipitant, and the suspension of the precipitate in the urine by means of mucilage. This mixture is then, after being diluted with water, poured into a vessel of certain capacity, which is placed over a white surface on which black lines are drawn. The amount of the "emulsified" urine necessary to obscure the lines will be in inverse ratio to the quantity of albumin in the urine, a quantity easily estimated by the employment of a suitably graduated burette. The principle is the same as that introduced by Panum for the determination of the quantity of cream in milk, and can no doubt be made available for clinical work. The results obtained are given in tables, but so far as can be gathered from these the advantage of the plan over that of Esbach (a far simpler method) does not seem very great; neither plan is quite accurate. W. D. H.

General and Physical Chemistry.

Relations between the Specific Rotatory and the Refractive Power of Chemical Compounds. Part II. By I. KANONNIKOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 686—693; compare this vol., p. 326). —In a former paper, the author has shown that very simple relations exist between the rotatory (α) and refractive (ϕ) powers of compounds of the same class, inasmuch as $\alpha = A\phi - B$, A and B being constants varying with each substance. Moreover, it was found that B/A = const. = 23·57, and $[\alpha]_D = A \times 5·6 = B/4·2$. With regard to the questions as to whether the value B/A has a special or a general significance, and whether it is possible to calculate the sp. rot. power from these constants A and B in the case of other substances, the author finds that the first relation holds good in the case of substances of perfectly unlike constitution:—

	A.	B.	B/A.
Nicotine	9·66	227·72	23·56
Tartar emetic	30·75	725·35	23·58
Quinic acid	7·40	174·56	23·59

The value B/A is found to change only with the nature of the solvent. Thus we have for solutions in ethyl alcohol—

	A.	B.	B/A.
Camphor	10·73	276·95	25·81
Russian turpentine	5·40	137·00	25·37
Coniine	2·65	69·80	26·34
Nicotine	20·77	537·50	25·87
Brucine	10·88	280·88	25·81
Menthol	10·61	273 00	25·73
		Mean	25·82

For solutions in chloroform, we have—

	A.	B.	B/A.
Camphor	31·12	1009·00	32·42
Terpene	30·80	999·79	32·46
Coniine	16·06	522·15	32·51
Menthol	61·43	1994·10	32·46
		Mean	32·46

The ratio $\alpha = A\phi - B$ then becomes $\alpha = A(\phi - c)$, where B/A = c = 23·57 for water, 25·82 for alcohol, and 32·46 for chloroform. These values are independent of the length of the rotating column.

The second question arises: What relation exists between the constants A and B and the sp. rot. power of active bodies? It is found that here again the relation varies with the nature of the solvent only, and that the general expression is—

$$[\alpha]_D = Ax \text{ and } [\alpha]_D = B/y.$$

Thus, for water $x = 5{\cdot}6$ and $y = 4{\cdot}2$, for alcohol $x = 5{\cdot}16$ and $y = 5{\cdot}00$, and for chloroform $x = 1{\cdot}78$ and $y = 18\ 21$.

It is remarkable, however, that the numbers calculated and found are sometimes identical, sometimes connected by a simple ratio, represented by such numbers as $\frac{1}{2}$, $\frac{1}{3}$, $\frac{3}{2}$, 2. The author proposes to investigate the influence of the chemical nature and properties of different compounds on the ratio B/A, and the cause of the variation above mentioned in the calculated rotatory power.

B. B.

Molecular Refraction. By W. SUTHERLAND (*Phil. Mag.*, [5], **27**, 141—155).—Newton's formula $(n^2 - 1)/d = c$, connecting index of refraction and density, Gladstone's $(n - 1)/d$, and Lorenz's $(n^2 - 1)/(n^2 + 2)d$, deduced theoretically from the assumption that in a medium composed of ether and molecules, light is propagated with a mean velocity but periodically varying amplitude of vibration, agree differently with experimental results. Thus Lorenz's formula holds good for both the liquid and gaseous states, but fails when change of density is produced by change of pressure, whilst Gladstone's meets the last requirement but fails to bridge over the great gap in density between liquid and vapour. Ketteler's theoretical formula, $(n^2 - 1)(v - \beta) = c(1 + ae^{-kt})$, where v = molecular domain and β = the true volume of the molecule, gives for compressibility results inferior to those obtained by Gladstone's formula. Lorenz's formula is derived by assuming a mean wave-length in the mixed medium, but this is erroneous, since the wave-length, as well as the amplitude, must vary as we pass from ether to matter. The author treats the velocities separately, and obtains a theoretical explanation of Gladstone's law. If the atoms are small and numerous, a ray will travel a certain mean distance in the atoms, which will represent a given loss of time and will be proportional to the length of path (s), the mean sectional area of the atom (a), and the number of atoms in unit volume d/m. If v is the velocity of light in free ether, V that in the atom, and l the mean distance through the atom, the loss of time in the atom will be $l/V - l/v$, and the total loss $= \frac{kslad}{m}\left(\frac{1}{V} - \frac{1}{v}\right)$, but this is equal to $\frac{s}{v'} - \frac{s}{v}$, where v' is the mean velocity of light in the medium, hence

$$\left(\frac{v}{v'} - 1\right)\frac{m}{d} = kla\left(\frac{v}{V} - 1\right),$$

that is, $(n - 1)m/d = kla(N - 1) =$ const., where n is the refraction index of the medium and N that of the atom. This is Gladstone's law. In the above considerations, the loss of time has been supposed to be due to the path through the atoms only. But the wave-point on issuing from the atom is a curved surface, and tends to recover its plane form in the intermediate ether, causing a further retardation, which is proportional to the length of path and is a function of the density, and as it vanishes with the density can be expressed by $s(bd + cd^2)$, where b and c are constants. The equation now becomes $(n - 1)m/d = la(N - 1) + m(b + cd +)$. In order to test this formula, the values at 10° and 20° (liquid) and at 100° (gaseous), determined by Lorenz (*Ann. Phys. Chem.* [2], **11**) for ethyl oxide, ethyl acetate, ethyl iodide, chloroform, and carbon bisulphide are examined. For this purpose, the above equation can be written

$$\frac{n - 1}{d} = \left(\frac{la(N - 1)}{m} + b\right) + cd.$$

c and the constant bracketed term can be determined from the values at 10° and 20°, and the bracketed term should agree with the value for the gas since cd vanishes, d being small. This is found to be the case, except for ethyl iodide.

Since Lorenz's formula gives the same value for liquids and vapours, and since for vapours $(n^2 - 1)/(n^2 + 2)d = \frac{2}{3}(n - 1)d$, it follows that the value of $(n - 1)/d$ for a vapour is $\frac{3}{2}$ of Lorenz's formula applied to the liquid. This fact is useful where a measurement at only one temperature is available, but may not always hold good.

H. K. T.

Spectral Analysis of Cadmium. By A. Grünwald (*Monatsh.*, **9**, 956—1034; compare Abstr., 1888, 389, 882).—The details of an analysis of the spectrum of cadmium by the method which has already been described by the author are here given. It is shown that cadmium contains condensation forms of the primary elements "*b*" and "*c*." The first is present in four different chemical conditions, namely, in the same condition as in helium, in that in which it occurs in free hydrogen, in that of combined hydrogen, as in water-vapour, and in a more condensed form than this latter. "*c*" occurs in two conditions: as found in oxygen, magnesium, and carbon, and in a less condensed state than the above.

In both zinc and cadmium "*b*" occurs in a more condensed condition than in water-vapour, the condensation for zinc being $\frac{5}{4}$ and for cadmium $\frac{7}{6}$. As zinc and cadmium occur in the same group in the periodic system, the first, however, in the fifth, the second in the seventh horizontal line, the author was led to believe that there might be some relation between the degrees of condensation in which "*b*" exists in elements belonging to the same group of the periodic system, expressible by "*b*" $\frac{n}{n - 1}$, where n is the number of the horizontal line in which the element having the above condensation form occurs. This has been confirmed for a number of elements. The opinion is also stated that the primary element "*c*" of oxygen is a definite condensation form of "*a*" of hydrogen.

The author replies to objections raised against his method, and expresses his firm conviction as to the general accuracy of his results.

H. C.

Gadolinium. By L. de Boisbaudran (*Compt. rend.*, **108**, 165—168).—Crookes's observations on the spectra of the fluorescences led him to conclude that Marignac's *gadolinium* is a mixture of 61 parts of yttria with 39 parts of samaria.* The term *yttria*, according to Crookes, denotes a mixture of earths which give different fluorescence spectra, and which form a family of very closely related substances, the equivalent of the metals oscillating about 89°. They all, however, give the same spark spectrum.

The author has previously shown that the principal fluorescence formerly attributed to yttrium is really due to $Z\alpha$ and $Z\beta$, which have atomic weights not less than 163, and therefore much higher than the atomic weight of yttrium. $Z\beta$ is probably identical with terbium. Moreover, it is not easy to see how a mixture of 61 parts of yttria ($Yt = 89$) with 39 parts of samaria ($Sm = 150$) could give an atomic weight of 156·75, which was found by Marignac to be the atomic weight of the metal in gadolinia.

The fluorescence of the earth formerly known as yttria is, when samaria is absent, practically identical with the fluorescence of a mixture of $Z\alpha$ and $Z\beta$, both of which have an atomic weight higher than that of yttrium and do not give the yttrium spark spectrum. Pure yttria shows the fluorescences of $Z\alpha$ and $Z\beta$ very feebly, but gives a magnificent spark spectrum. The author applies the term yttria to the non-fluorescent substance which gives the well-known yttrium spark spectrum, and is the oxide of a metal with an atomic weight of about 89.

Comparison of the spark and fluorescence spectra of Marignac's gadolinia with those of mixtures of yttria with varying proportions of other rare earths, leads to the conclusion that it contains a distinct oxide *gadolinia*, with the following impurities:—

Di_2O_3.	$Z\beta_2O_3$.	Yt_2O_3.	Sm_2O_3.	$Z\alpha_2O_3$.	CaO.
0·24	4·70	0·15	4·40	0·13	0·07

The small quantities of $Z\beta$ and samaria still remaining must be regarded as the residue of impurities which would be completely removed by appropriate fractionation. The greater part of the gadolinia has resisted a fractionation sufficient to remove almost all the yttrium and $Z\alpha$, and hence, if it is still compound, it must contain hitherto unknown elements which are extremely difficult to separate.

C. H. B.

Chemical Theory of the Galvanic Element. By F. Exner and J. Tuma (*Monatsh.*, 9, 903—943).—The authors show that the results obtained by Ostwald (Abstr., 1888, 886) with dropping electrodes of mercury are untrustworthy, inasmuch as two sources of error remain unnoticed, the first being chemical action of the electrolyte on the mercury, and the second the subsequent occurrence of polarisation. It was found experimentally that the first in the case of dilute sulphuric acid makes as large a difference as 0·84 Daniell on the result, and the second 0·8 to 1·2 Daniell. The two being, however, of opposite sign, tend to neutralise one another. These errors also occur in the observations of Moser and Miesler (Abstr., 1888, 209, 392).

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* The statement as to gadolinium made at the commencement of this paper entirely misrepresents Crookes's views on the subject (compare *Proc. Roy. Soc.*, 40, 502, and *Chem. News*, 54, 39).—Ed.

An arrangement is then described in which these sources of error are eliminated, the mercury being allowed to drop into a cylinder of filter-paper, wetted with and connected by a damp thread to the solution in which dips the metal under examination. A number of metals in different solutions were examined, and in every case, with the apparent exception of carbon and platinum in concentrated nitric acid, the metal was found to be negatively charged. The exception is ascribed to the formation of nitrous acid in solution. It also appears that the numbers obtained for metals in acids are identical with those for the same metals in salts of the same acids.

Details of experiments on the potential differences in galvanic cells and voltameters are also given. H. C.

Electric Conductivity of Fused Salts. By L. POINCARÉ (*Compt. rend.*, **108**, 138—141).—The addition of a small quantity of silver nitrate to any fused nitrate depolarises immediately and completely a silver electrode which is immersed in it. If such an electrode is placed in fused silver nitrate, and then thoroughly washed with water, it remains depolarised for some time when immersed in a fused alkaline nitrate. It is therefore possible in certain cases to simplify the method devised by Bouty and the author for determining the conductivity of fused salts, and it has been applied to fused silver nitrates and mixtures of this salt with other nitrates.

The specific conductivity of fused silver nitrate between 280° and 370° is represented by the expression $Ct = 1·233 [1 + 0·0025(t - 350°)]$. Experiments with five mixtures through a somewhat wide range of temperature give results which are represented by the formula—

$$C''_t = \frac{pc_{350} + qc'_{350}}{p + q}\left[1 + \frac{p^{\alpha} + q\beta}{p + q}(t - 350)\right],$$

in which p and q are the volumes, and not the weights of the respective salts, and α and β the coefficients of variation with the temperature. The conductivity of ammonium nitrate is given by the equation $\gamma_t = 0·400 [1 + 0·0073(t - 200)]$.

In the case of the nitrates of sodium, potassium, silver, and ammonium, the coefficients of variation with the temperature are inversely as the sp. gr. of the corresponding salts. The molecular conductivities of the potassium and ammonium salts, 0·0397 and 0·0420 respectively, are almost identical, whilst those of silver nitrate, 0·0537, and sodium nitrate, 0·0602, show considerable differences. It is noteworthy that the first two give solutions with normal properties, whilst the solutions of the second two show abnormal behaviour.

C. H. B.

Abnormal Electromotive Forces. By E. F. HERROUN (*Phil. Mag.* [5], **27**, 209—233).—The author investigates those cells in which the electromotive forces do not agree with the theoretical values as deduced from thermochemical data. The method consists in passing a current between electrodes immersed in solutions of their salts separated by a porous cell, and noting the changes of temperature in the solutions. The results lead to the conclusion that the electromotive force is derived from the free energy of the chemical process. If a portion of the total energy (as measured by the calorimeter) is negative, this may be supplied at the expense of either the free or bound energy. In the first case there will be a reduction in electromotive force, whilst in the second the effect will be simply thermal. Thus with silver nitrate solution, whilst the total energy is 27600 — 10880 = 16720, the electromotive force corresponds to 27600 thermal units, the —10880 (heat of solution) being supplied by the disappearance of sensible heat. The author questions Helmholtz's view that mercury deposited by zinc, even from its solid salts, can give an electromotive force in excess of thermal values. In the case of hydrated salts, the electromotive force does not incorporate the whole heat of hydration, it is therefore only in the case of salts which do not form hydrates, and consequently only absorb heat during solution, that the electromotive force is equivalent to the heat of formation of the solid salt. It is not yet determined whether there is any relation between that portion of the heat of hydration which is converted into electrical energy and that which runs down into heat. In some cases (zinc-cadmium chloride cell) the degradation of energy increases with the dilution of the salt solution. The above makes it apparent that no cell can give an electromotive force in excess of the free energy of the reaction, and negatives the possibility of the conversion directly of sensible heat into electrical energy. Low electromotive forces are in many cases due to the formation of films, or sub-salts, on the surface of the metals, thereby leading to a different thermochemical reaction. H. K. T.

Electrolysis of Copper Chloride. By F. QUINCKE (*Ann. Phys. Chem.* [2], **36**, 270—272).—According to Faraday's law, the quantities of different substances separated at the electrodes are in the ratio of their chemical equivalents. Therefore in the case of compounds of the higher and lower oxides of a metal, different quantities of the metal will be separated at the cathode for the same amount of anion set free at the anode, so that the chemical equivalent must have more than one value.

The only direct experimental proof of this result, not obviously vitiated by secondary actions, was given by Buff, who passed a current through a copper voltameter and a tube containing fused copper chloride connected in series, so that both were traversed by the same current. He found that the diminution in weight of the copper anode in the copper sulphate was about half as much as the diminution of the anode in the fused chloride, but was unable to obtain any accurate determination of the increase in weight of the anode in the fused chloride.

The author has repeated this experiment, and finds that no definite conclusions can be drawn from it, as the copper electrode in the fused chloride was found to dissolve gradually when the battery was cut out of the circuit, owing to the production of a current of sufficient strength to be indicated by an ordinary tangent galvanometer. This current was very irregular, and the author attributes it to inequalities in the temperature of different portions of the fused salt.

G. W. T.

Heat Conductivity of Mixtures of Ethylic Alcohol and Water. By H. HENNEBERG (*Ann. Phys. Chem.* [2], **36**, 146—164).—In 1880, Weber showed that the ratio of heat conductivity to the specific heat of unit volume was the same for all the liquids experimented with. In 1885 (*Berlin Monats.*) Weber obtained another and more complex law, namely, if k is the heat conductivity of the liquid, c its specific heat, and ρ its density, μ the number of molecules in the state of vapour which make up a single molecule of the liquid, λ^3 the volume of such a molecule, then the quantity $\frac{k}{c\rho} \cdot \frac{\lambda}{\sqrt[3]{\mu}}$ is constant for all liquids of similar chemical constitution.

The author transformed this expression by means of the relation $\lambda / \sqrt[3]{\mu} = \sqrt[3]{m/\rho}$, where m is the mass of a molecule of the liquid: a relation which is obtained immediately, since if N is the number of molecules of liquid in unit volume, $\rho = \mathrm{N}\mu m$ and $\mathrm{N}\lambda^3 = 1$.

He then found that although the values of the heat conductivity were in all cases included between the values for pure water and pure alcohol respectively, the heat conductivity of the mixtures did not obey either of Weber's laws, from which he considers it probable that such mixtures consist each of one or more chemical compounds, and that the compounds occurring in the different mixtures are not identical.

G. W. T.

Specific Heats of Gases at Constant Volume. By J. JOLY (*Proc. Roy. Soc.*, **45**, 33—36).—Two equal thin metallic spheres are suspended from a delicate balance in separate steam calorimeters, their thermal capacities being made equal by the addition of copper wire, so that the condensation on each is equal, and the balance remains in equilibrium. Air is now forced into one, and their specific heats again compared by means of the formula $\mathrm{S} = \frac{w\lambda}{\mathrm{W}(t_2 - t_1)}$, where λ is the latent heat of steam, w the weight of steam condensed, W the weight of gas, and t_2, t_1 the extremes of temperature. Concordant results are obtained which are slightly above the value usually assigned. The results show that the specific heat is quite independent of the compression of the air. The reason of the excess over the theoretical value is not apparent.

H. K. T.

Heats of Formation of several Organic Acids. By I. OSSIPOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 650—652).—The following preliminary values were found as the heats of combustion of—

Sorbic acid............	726·6— 731·3 Cal.
Terebic acid...........	791·0— 787·6 „
Cinnamic acid.........	1032·6—1024·3 „
Atropic acid..........	1042·4—1043·2 „

B. B.

Heats of Combustion of Stilbene and the Isomeric Nononaphthenes. By I. Ossipoff (*J. Russ. Chem. Soc.*, 1888, **20**, 645—650).—The heats of combustion of stilbene and the two isomeric nononaphthenes, C_9H_{18}, obtained by Markownikoff from Caucasian petroleum, were determined by means of the "calorimetric bomb." The results obtained are—

Stilbene, m. p. 124—125°.......	1771·7 Cal. const.	volume.
	1773·3 „ „	pressure.
Nononaphthene, b. p. 135—136°.	1380·9 „ „	volume.
	1383·4 „ „	pressure.
Isononaphthene, b.p. 150—151°	1381·7 „ „	volume.
	1384·2 „ „	pressure.

B. B.

Dilatation and Compression of Air. By C. Antoine (*Compt. rend.*, **108**, 141—144).—A mathematical paper not admitting of useful abstraction.

Velocity of Sound in Vapours and the Determination of the Vapour-density. By W. Jaeger (*Ann. Phys. Chem.* [2], **36**, 165—213).—The velocity of sound in a perfect gas is given by the equation $V = \sqrt{gk\frac{R}{d}T}$, where g is the acceleration of gravity, k the ratio of the specific heat at constant pressure to the specific heat at constant volume, T the absolute temperature, R the gaseous constant for air, and d the relative density of the gas.

The author makes use of this relation to determine the densities of the superheated vapours of ether, alcohol, and water at various temperatures. He also determines the ratio of the specific heats for these three vapours, and finds that in ether vapour $k = 1·097$, for alcohol vapour $k = 1·133$, and for steam $k = 1·33$. G. W. T.

Vapour-density Determinations. By T. W. Richards (*Chem. News*, **59**, 87—88).—The author points out that when using apparatus in which vapour-densities are measured by the fall of a column of mercury in an attached barometer tube, errors due to cooling in the unheated parts of the apparatus may be eliminated by reducing the extent of those parts, and an apparatus for the purpose is described. D. A. L.

Relation between the Solubility of Salts and their Melting Points. By A. Etard (*Compt. rend.*, **108**, 176—178; comp. Abstr., 1888, 548).—The solubility of many salts increases with the temperature up to the melting point of the anhydrous salt, and beyond this point a given quantity of water can dissolve an unlimited quantity of the salt.

Potassium nitrate:—Between 0° and 10° the line of solubility is slightly curved, but beyond 10° the solubility is represented by the following expressions:—From 10° to 69°, $y = 17{\cdot}0 + 0{\cdot}7118t$; from 69° to 125°, $y = 59{\cdot}0 + 0{\cdot}375t$; from 125° to 338°, $y = 80{\cdot}0 + 0{\cdot}0938t$.

Sodium nitrate:—From −15° to 64°, $y = 36{\cdot}0 + 0{\cdot}2784t$, and from 64° to 313°, $y = 58{\cdot}0 + 0{\cdot}1686t$.

Potassium chlorate:—From 0° to 42°, $y = 2{\cdot}6 + 0{\cdot}2000t$; from 42° to 171°, $y = 11{\cdot}0 + 0{\cdot}3706t$, and from 171° to 359°, $y = 59{\cdot}0 + 0{\cdot}2186t$.

Silver nitrate:—From 55° to 198°, $y = 81{\cdot}0 + 0{\cdot}1328t$.

Barium nitrate:—From 0° to 210° $y = 4{\cdot}5 + 0{\cdot}2000t$.

The curve of solubility being the locus of the melting points of mixtures of the anhydrous salts and water, the solubilites at temperatures between 200° and 450° were determined by observing the temperatures at which the salt melted in mixtures of the salt and water of known composition. C. H. B.

General Law of Diminution of Volume of Salts by Solution in Water.

By A. Heritsch (*Ann. Phys. Chem.* [2], **36**, 115—122, and *J. Russ. Chem. Soc.*, 1888, **20**, 632—645).—If δ is the diminution of volume due to the formation of 100 grams of solution, p the percentage weight of the salt, it can be shown that $\delta = C(100 - p)p$, where C is a constant for a given temperature. This expression attains a maximum for $p = 50$. Also since $(100 - p)p > \frac{(100 - 2p)2p}{2}$, it follows that contraction must always take place during solution, which is in agreement with experiment.

The author has determined the coefficient C for the chlorides of sodium, potassium, ammonium, aluminium, strontium, barium, calcium, magnesium, and zinc; the nitrates of sodium and potassium, the sulphates of potassium, sodium, ammonium, magnesium, and zinc; the bromides of ammonium and potassium; the carbonates of sodium and potassium; potassium acetate, magnesium and potassium sulphates, potassium hydroxide, potassium oxalate, tartaric acid, citric acid, phosphoric acid, copper sulphate, lithium chloride, and ammonium nitrate.

Except in the case of the last two, he finds the formula to be true. In the case of these two salts, δ is greater for weak than for strong solutions. The author attributes this to dissociation taking place after a certain amount of dilution. G. W. T.

Influence of Temperature on Evaporation and on the Diffusion of Vapours.

By A. Winkelmann (*Ann. Phys. Chem.* [2], **36**, 93—114).—If D_0 and D_t are the coefficients of diffusion of a pair of gases at 0° and t° respectively, and A is the coefficient of expansion of a gas, the relation between D_t and D_0 may be expressed by an equation of the form—

$$D_t = D_0 (1 + at)^m.$$

The author finds the following values for the constant m—

Gases.	m.
Air and carbonic anhydride	1·968
Oxygen and hydrogen	1·755
Oxygen and nitrogen	1·792
Steam and carbonic anhydride ...	1·972
Steam and hydrogen............	1·712
Steam and air	1·774

Now if η_0 and η_t are the viscocity coefficients of a gas at 0° and t° respectively—

$$\eta_t = \eta_0(1 + at)^n.$$

Also by the kinetic theory of gases—

$$D_t = D_0(1 + at)^{n+1},$$

which gives $m = n + 1$.

The theoretical value of n is 0·5, but its value as determined by the most trustworthy experimental methods approaches more nearly to unity. This may be explained by supposing that the length of the free path of the molecules increases with the temperature. Stefan and O. E. Meyer have attributed this to a closer approach of the mutually impinging molecules at higher than at lower temperatures.

The values obtained for the constant m if they are trustworthy, therefore, show that the molecule of water behaves like the molecules of oxygen and nitrogen, and that the radius of the sphere of mutual action diminishes less rapidly with increasing temperature in the case of water molecules than in the case of molecules of carbonic anhydride. The author suggests that it would be of interest to investigate vapours of complex molecular structure, to see whether, as would be anticipated, the constant m has relatively high values in such cases.

G. W. T.

Gradual Chemical Change. By W. H. PENDLEBURY and M. SEWARD (*Proc. Roy. Soc.*, **45**, 124—126).—Mixtures of chloric and hydrochloric acids and of potassium chlorate and hydrochloric acid were made, potassium iodide added, and the rate at which iodine was set free determined by means of sodium thiosulphate. The rate of liberation of iodine represents the velocity of reaction of the acids, the decomposition of the potassium iodide being comparatively instantaneous. With variation of chloric acid, the rate varies, (1) directly, as a participant in the reaction, (2) with a small acceleration proportioned to the amount present. With variation of hydrochloric acid there is observed (1) a secondary (accelerative) effect on the decomposition of chloric acid by itself, and (2) an effect both primary and secondary on the decomposition of chloric acid with hydrochloric acid. With potassium chloride present there is a small accelerative effect proportional to its quantity. Temperature and velocity are related, so that the latter increases in geometric progression when the former increases in arithmetical progression. H. K. T.

Reduction-velocity of Alkaline Copper Solutions. By F. URECH (*Ber.*, **22**, 318—319).—The author gives a table showing that the formula $kw^y = u^x . t$ where k = constant (compare *Ber.*, **17**, 495), can be employed for the comparison of analogous reactions and for calculating the coefficients appertaining thereto. If m is the number of molecules of copper sulphate acting on one molecule of dextrose, the differential velocity formula under the simplest conditions is $kuv^m . dt = -du = ku^n dt$ for $v = u$, and integrated $kt = lgu_0 - lgu$. The experimental results previously published (*loc. cit.*) do not agree with this integral formula, but it is shown by a table that by introducing a term (d) for correction of time, the results agree somewhat better with the integral formula $k(t + d) = lgu_0 - lgu$, where $d = 6$, although several influences cannot as yet be formulated.

F. S. K.

A General Method of Estimating the Basicity of Acids. By F. Fuchs (*Monats.*, 9, 1132—1142).—Sodium hydrosulphide and potassium hydrosulphide can both exist in aqueous solution, and are perfectly stable when the solution is surrounded by an atmosphere of hydrogen sulphide. Making use of the well-known fact that hydrogen sulphide can be turned out of combination by even the feeblest acids, the author explains a method of determining the basicity of an acid by estimating the amount of hydrogen sulphide a known weight (0·05—0·06 gram) of the acid can liberate from an alkaline hydrosulphide, the amount set free being ascertained either by absorbing the gas in soda and subsequent neutralisation with acetic acid and titration with iodine, or by allowing the gas to react with mercury and directly measuring the volume of hydrogen set free.

G. T. M.

Prout's Hypothesis, especially with reference to the Atomic Weights of Carbon and Oxygen. By J. A. Groshans (*Rec. Trav. Chim.*, 7, 358—364).—The author shows that isomeric organic compounds, containing carbon, hydrogen, and oxygen, which have the same molecular weight but different composition, belong to one of seven general series, the molecular weights in each of which are given by $14n + 2x$, where x is any unit less than 7. He argues from the equality in the molecular weights of such compounds of different composition, that the atomic weights differ by some multiple of that of hydrogen, so that $C + 4 = O$ and $4C = 3O$, and hence that $C = 12$ and $O = 16$.

H. C.

Sublimation Apparatus. By J. W. Brühl (*Ber.*, 22, 238—240).—The author describes, with the aid of a diagram, an apparatus designed for purifying substances by sublimation. The apparatus employed for substances melting at a comparatively low temperature, consists of a flat, circular, brass box (B), supported on a iron tripod and provided with an inlet and an outlet tube so that it may be kept cool by means of a constant stream of water. In the centre of this box there is a perforation shaped like the segment of a cone, the base being downwards. The crucible containing the substance is placed in the hole in the box (B) and a flat, well-fitting, glass bell-jar is placed on the box; as the only part of the crucible in contact with (B) is a very narrow circular surface, a very small flame is sufficient to heat the crucible. The crucible should be made of some metal which is a good conductor of heat; if the glass cover is moderately flat almost the whole of the substance condenses on the cool brass surface. This apparatus can also be suitably employed for fractional sublimation.

Another form of apparatus for substances melting at a moderately high temperature, consists of an ordinary flat, porcelain plate, in the centre of which a small circular hole is made to hold the crucible, and a flat, well-fitting, glass bell-jar cover. The plate is kept cool by a circular piece of asbestos card, which is placed in the hollow of the plate, and a square, somewhat larger piece which rests directly on the tripod; both layers of asbestos are pierced in the centre and soaked in cold water before the commencement of the operation. F. S. K.

Apparatus for Crystallising at a Low Temperature and in Absence of Moisture and Air. By J. W. Brühl (*Ber.*, 22, 236—238).—The apparatus described, a diagram of which is given, was employed by the author for crystallising substances at a low temperature in a perfectly dry atmosphere or in absence of both moisture and air. The apparatus can also be employed for saturating liquid with gaseous substances at a low temperature and separating the solid products in a pure condition.

The liquid is placed in a thick, wide glass tube (B), the lower extremity of which is funnel-shaped and connected with a narrow glass tube (*b*), the upper end being covered with a very small, shallow, glass bell-jar, and made air-tight by means of a thick ring of soft india-rubber which surrounds the tube (B). The bell-jar is provided with a tubulus and india-rubber cork, through which passes a chloride of calcium tube; the latter is either closed by means of a pinch-cock (*p*), or, if a gas is to be passed into the apparatus, it is connected with the conducting tube. The receiver (B) is surrounded by a small inverted bell-jar (A) containing the freezing mixture. The narrow tube (*b*), with which (B) is connected, passes somewhat loosely through an india-rubber cork in the tubulus of the bell-jar (A), as does also a tube, bent at a right angle and provided with a pinch-cock, through which the freezing mixture can be run off at the end of the operation. A platinum cone, pierced with a small hole, is placed in the funnel-shaped portion of the tube (B), and the narrow tube (*b*), in connection with (B), is drawn out to a smaller diameter and connected by india-rubber tubing with a glass tube (D), provided with a stopcock (*h*). The lower extremity of (D) passes through an india-rubber cork, fitting into a small flask (E), which is provided with a tubulus. The apparatus is employed as follows:—The stopcock (*h*), being closed, a few drops of the liquid are placed in (B) to make the platinum cone adhere to the glass, and the whole of the liquid is then poured in; the bell-jar cover (C) is made air-tight, and the receiver (B) and the portions in connection therewith are lowered into the vessel (A), so that when the freezing mixture is placed in (A) only the bell-jar cover remains above the surface. When the separation of crystals is at an end, the calcium chloride tube is closed by the pinch-cock (*p*), the cock (*h*) is opened, and the whole apparatus is exhausted as completely as possible by connecting the tubulus of (E) with the pump. Dry air can then be passed through the apparatus by slowly opening the pinch-cock (p). If oxygen is to be excluded, the apparatus is filled with some indifferent gas before the commencement of the process, and, when the operation is at an end, the same gas can be passed through the apparatus by connecting the conducting tube with the calcium chloride tube. F. S. K.

Inorganic Chemistry.

Preparation of Hydrogen. By J. HABERMANN (*Zeit. anal. Chem.*, **28**, 88).—A granulated alloy of tin and zinc, containing about 83 per cent. of the latter, prepared by adding zinc to molten tin as long as it dissolves, is recommended for use in Kipp's apparatus. The pieces retain their shape and size after all the zinc is dissolved out, and therefore have no tendency to fall through into the lower bulb.

M. J. S.

Preparation of Oxygen. By C. F. GÖHRING (*Chem. Zeit.*, **12**, 1659—1660).—It is proposed to prepare oxygen by adding potassium permanganate to hydrogen peroxide made alkaline with ammonia.

D. A. L.

Combustion in Dried Oxygen. By H. B. BAKER (*Proc. Roy. Soc.*, **45**, 1—3).—This paper is a continuation of the author's experiments on combustion in dry oxygen (Trans., 1885, 349). The elements were very carefully purified, especially from occluded hydrogen. Carbon, sulphur, boron, and phosphorus were found to have their combustion arrested in proportion to the dryness of the oxygen. In no case when the materials were carefully dried, did flame appear.

In experiments with amorphous phosphorus, it was found that when heated in nitrogen up to 300°, no change into the ordinary modification took place, whilst in moist oxygen, combustion commenced at 260°, hence amorphous phosphorus burns as such and is not first converted into the ordinary form as is generally supposed.

Carbon burnt in partially dried oxygen mainly gives rise to carbonic oxide even at temperatures at which carbonic anhydride cannot be reduced by carbon. Hence carbonic oxide is the first product in the combustion of carbon, further oxidation, in this particular case, being prevented by the dryness of the oxygen. Carbonic oxide is also produced by the slow combustion of carbon in air at 440°, a temperature too low for a reduction of carbonic anhydride to have taken place.

H. K. T.

Valency of Boron. By G. GUSTAVSON (*J. Russ. Chem. Soc.*, 1888, **20**, 621—623).—Referring to Lorenz's paper (Abstr., 1888, 1246), in which the author says that the product of the action of equivalent quantities of boric anhydride and boron trichloride is not BOCl, "as assumed by Gustavson," Gustavson shows that in his original paper (in Russian), he never said that the compound produced had the composition BOCl, for this would be absurd, as half of the boron trichloride employed was distinctly said to escape on heating. As he obtained substances differing widely in composition, he believed it to be right to assign no formula to the product; Lorenz, on the other hand, although his results varied greatly: $B_2O_3 = 74·8—82·5$ and $Cl = 20·2—24·2$, took the mean result as correct, from which he deduced the formula $B_8O_{11}Cl_2$: this is evidently of no great value.

B. B.

Formation of Carbon Oxysulphide. By C. BÖTTINGER (*Ber.*, **22**, 306).—A claim of priority.

Relative Rates of Dissolution of Gypsum and Anhydrite. By J. F. MCCALEB (*Amer. Chem. J.*, **11**, 31—33).—Owing to the difficulty of pulverising selenite completely, the solvent action of water on the various specimens experimented with was determined by immersing blocks of the minerals. Only a portion, about 6—9 sq. cm., of one smooth surface was exposed, the other parts being covered with a layer of paraffin. The blocks were suspended just below the surface of 4 litres of distilled water in tall jars. The temperature varied from 19° to 32°. The specimens used were as follows:—A, gypsum, "pure" pink, micaceous mass; B, gypsum, "pure" white massive; C. selenite, "pure" honey-yellow crystal; D, anhydrite, "impure" grey massive; E, anhydrite, "pure" greyish massive; F, gypsum and anhydrite mixed, white massive.

Amounts of calcium sulphate in grams dissolved from each square centimetre of surface in one week:—

A.	B.	C.	D.	E.	F.
0·2388	0·2219	0·1177	0·0666	0·0601	0·2184

In order to determine the rate at which the solvent acts as it becomes more nearly saturated, the pieces B, C, D were exposed for a longer time and afforded the following results:—

	1st week.	2nd week.	3rd week.	4th week.	5th week.
B	0·2219	0·4638	0·6788	0·8168	0·8768
C	0·1177	0·2021	0·3250	0·4179	0·4893
D	0·0666	0·0999	0·1514	0·1881	0·2398

J. W. L.

Hydration of Calcium Sulphate. By J. F. MCCALEB (*Amer. Chem. J.*, **11**, 34—35).—In order to determine the rate at which anhydrous calcium sulphate becomes converted into the hydrate, three specimens were experimented upon. D, an impure anhydrite from Salzberg; E, a pure anhydrite from Nova Scotia; G, a pure selenite from Montmartre, which was heated to bright redness.

Portions of 1 gram of these various specimens, in a state of fine division, were moistened on watch-glasses with water and placed under a bell-jar over water. In order to determine the extent of hydration, the watch-glasses and contents were dried over sulphuric acid and weighed, only mechanically admixed water being given off under these circumstances. The results were as follows:—

	1 week.	2 weeks.	3 weeks.
D	0·0209	0·0357	0·0493
E	0·0072	0·0155	0·0234
F	0·0022	0·0048	0·0073

The temperature during this series of experiments varied between 20—25°. Also a number of watch-glasses, each containing 1 gram of anhydrite D, were exposed to moisture in a similar manner, the temperature being about 25—30°:—

	No. of weeks exposed.						
	4.	8.	12.	16.	20.	28.	36.
Water absorbed	0·0308	0·0488	0·0629	0·0700	0·0803	0·0873	0·0949

J. W. L.

Specific Gravity of Calcium Sulphate. By J. F. McCaleb (*Amer. Chem. J.*, **11**, 35—36).—These determinations were made by means of the specific gravity bottle, with a paraffin oil of high boiling point. The specific gravity is stated in reference to water at 15°.

(1) "Plaster of Paris," obtained by heating crystallised selenite to 200°; sp. gr. = 2·577. (2) Same selenite heated to a dull red heat; sp. gr. = 2·911. (3) Same selenite heated to a bright red heat; sp. gr. = 2·890. (4) Same selenite heated on platinum until just melted; sp. gr. = 2·796. (5) Same selenite heated in clay crucible in a blast furnace; sp. gr. = 2·654. (6) Anhydrite (97 per cent. pure); sp. gr. = 2·907. According to Clark, selenite has sp. gr. = 2·30—2·33; anhydrite has sp. gr. = 2·92—2·98. J. W. L.

A Red Copper Slag containing Artificial Cuprite. By J. L. Jarman and J. F. McCaleb (*Amer. Chem. J.*, **11**, 30—31).—The specimen examined was from the Canton copper works of Baltimore. It is very hard and tenacious, breaks with conchoidal fracture and splintery edges, and contains minute beads of copper disseminated through its mass. It is opaque with dark scarlet colour. Sp. gr. = 3·486. H = 4·8.

The analysis gave the following figures:—

SiO_2.	Cu_2O.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.
38·039	47·489	2·001	2·829	2·525	0·404	0·549	5·920

Under the microscope it appeared as a transparent matrix of a pale-yellow colour, in which minute transparent crystals of a cochineal colour, mostly of cubical and rectangular forms, were observed.

Treated with 8 per cent. nitric acid in a very finely pulverised condition, 46·29 per cent. was dissolved, and of this 43·49 per cent. was cuprous oxide. The resulting pale-yellow powder contained no red fragments. From this it appears that the red particles consist of cuprous oxide, and they appear to be in the form of the native cuprite (Brown, *Amer. J. Sci.*, **32**, 379). The yellow powder is insoluble in aqua regia and sodium hydroxide; sp. gr. = 2·31; H = 4·8, fusible without change of colour, but in the oxidising flame it forms a blue glass.

The analysis gave—

SiO_2.	Al_2O_3..	FeO.	CaO.	MgO.	Cu_2O.	K_2O.	Na_2O.
69·22	4·84	5·74	3·33	0·89	5·65	0·61	10·34

J. W. L.

Affinity of the Heavy Metals for Sulphur. By E. Schürmann (*Annalen*, **249**, 326—350).—An investigation of the action of solutions of various metallic salts on 16 metallic sulphides led to the following results :—Palladium sulphide is not attacked by any of the metallic salts, and palladium dichloride decomposes all metallic sulphides. Manganese sulphide is the least stable of the 16 sulphides examined. Arranged in the order of their affinity for sulphur, the metals form the following series :—Pd, Hg, Ag, Cu, Bi, Cd, Sb, Sn, Pb, Zn, Ni, Co, Fe, As, Tl, Mn. In each natural family of elements, the affinity to sulphur increases with the atomic weight. Family IV is an exception to this law, as the affinity of sulphur to tin is greater than its affinity to lead. The members of family III have less affinity to sulphur than their neighbours in family IV, and these again than the corresponding elements with a slightly higher atomic weight in family V. W. C. W.

Interaction of Chromic Acid and Hydrogen Peroxide. By Berthelot (*Compt. rend.*, **108**, 157—161).—When hydrogen peroxide is added to a solution of a dichromate acidified with a strong acid, the blue compound is formed and a slow evolution of oxygen begins almost immediately, the chromium being reduced to the form of a chromic salt. The ratio of the oxygen liberated from the chromic acid to that liberated from the peroxide is 1 : 1 when the hydrogen peroxide is added to the chromium solution, and 3 : 5 if the order of addition is reversed. Decomposition takes place more rapidly in presence of nitric acid than in presence of sulphuric acid.

When the dichromate solution is acidified with a feeble acid, such as acetic or phosphoric, it first acquires, according to the degree of concentration, a violet or purple colour, which is due to a mixture or compound of the perchromic acid and a brown substance. The oxygen ratios are the same as with the strong acids. With still feebler acids, such as boric or hydrocyanic, the brown substance alone is formed, and the rate of decomposition is very slow. The phenomena are, in fact, similar to those observed with hydrogen peroxide and a solution of pure chromic acid.

If the peroxide is added to a moderately strong solution of chromic acid, the liquid is at first blue and then becomes violet, brown, or even green, but with very dilute solutions at a temperature not exceeding 10°, mere traces of perchromic acid are formed, and the brown substance is the chief product. The same results are obtained with potassium dichromate, which has been mixed with an exactly equivalent quantity of hydrochloric or sulphuric acid.

The action is most regular with a solution of pure potassium dichromate, which may be regarded as a mixture of normal chromate with chromic anhydride. If a solution of this salt containing a gram-molecule in 16 litres is mixed with an equivalent quantity of a solution of hydrogen peroxide which contains a gram-molecule in 2 litres, the liquid darkens in colour, rapidly becoming a very deep brown, and oxygen is liberated with effervescence, but during this reaction, the liquid contains mere traces of perchromic acid. After some time, the liquid becomes clear and has its original tint; it then contains neither hydrogen peroxide nor reduced chromium oxide. In the calorimeter, the temperature rises gradually, and after four minutes the reaction is practically complete, the heat liberated being +20·8 Cal., a number almost identical with the heat liberated by the decomposition of hydrogen peroxide, namely, +21·6 Cal. Indeed, if the final reading is taken 19 minutes after mixing, the total heat liberated is 21·4 Cal.

The same quantity of potassium dichromate will decompose in the same manner an unlimited quantity of hydrogen peroxide.

The brown intermediate product is probably a compound of hydrogen peroxide with chromic oxide: it decomposes rapidly, with regeneration of chromic acid, liberation of oxygen, and formation of water. As the thermal measurements show, the heat liberated by the reaction is identical with that liberated by the decomposition of hydrogen peroxide.

The brown colour of the intermediate product points to the formation of chromium chromate, which is probably combined with hydrogen peroxide, thus: $(n + 2)CrO_3 + 6H_2O_2 = nCrO_3,Cr_2O_3,3H_2O_2 + 3H_2O + 3O_2$. The peroxide then oxidises the chromium chromate with reproduction of chromic acid and formation of water.

A solution of normal potassium chromate containing a gram-molecule of the salt in 4 litres, at first shows no change when mixed with hydrogen peroxide, but after some time decomposition takes place in the same manner as with the dichromate, although very much more slowly. After the decomposition, all the chromium is still present as chromate. This reaction may be explained by the fact that in solution, potassium chromate is partially dissociated into potassium dichromate and potassium hydroxide, the latter accelerating the decomposition.

Unlimited decomposition, the formation of an unstable intermediate compound, and the liberation of heat owing to the decomposition of some endothermic compound, are characteristic of all the so-called "actions of presence." C. H. B.

Phosphotungstic Acid. By C. H. Brandhorst and K. Kraut (*Annalen*, **249**, 373—380).—The sp. gr. at 20° of solutions of sodium phosphotungstate, $2Na_2O,P_2O_5,24WO_3 + 27H_2O$, is shown in the table (p. 470).

Phosphotungstic acid is obtained in the free state by adding to a solution of the acid sodium salt, in half its weight of water, one-tenth its volume of strong hydrochloric acid. The free acid is extracted from the mixture by ether free from alcohol. It can also be obtained by adding strong nitric acid to a solution of the sodium salt. The precipitate is redissolved in water, and reprecipitated by nitric acid

Percentage.	Sp. gr. crystallised salt.	Sp. gr. anhydrous salt.
5	1·04	1·044
10	1·084	1·092
15	1·131	1·143
20	1·181	1·199
30	1·299	1·333
50	1·64	1·734
64	1·998	—

three times. Finally it is recrystallised from a mixture of nitric acid and water. The crystals belong to the rhombic system, and contain 93 mols. H_2O, the formula being $48WO_3,2P_2O_5 + 93H_2O$. Acid sodium phosphotungstate dissolves precipitated barium carbonate, forming a crystalline salt of the composition

$Na_2O,2BaO,P_2O_5,24WO_3 + 46H_2O$. W. C. W.

Mineralogical Chemistry.

Pyrolusite from Augusta Co., Virginia. By J. L. JARMAN (*Amer. Chem. J.*, **11**, 39—40).—The larger portion of the ore of the Crimora mine consists of psilomelane, with about one-third as much pyrolusite. The following analysis was made of portions from a fine mass of the ore weighing upwards of 50 lbs. It consists of a network of fibrous crystals, closely matted; colour, grey; streak, black; H. = 2·7; sp. gr. 4·69; infusible—

MnO_2.	Fe_2O_3.	CaO.	NiO.	CoO.	K_2O.
95·88	0·617	0·094	0·225	0·269	0·179

Na_2O.	H_2O.	Insoluble residue.
0·232	2·085	0·293

J. W. L.

Beryllonite. By E. S. DANA and H. L. WELLS (*Amer. J. Sci.*, **37**, 23—32).—The authors give a more complete account of the new mineral recently described by E. S. Dana (this vol., p. 355). The first specimens were discovered in 1886 near Stoneham, Maine. The specimens are mostly fragments of crystals. Well-formed crystals are rare. Twins are common, the twinning plane being a prism of about 60°. The measured angles and optical characters conform to the orthorhombic system, the axial ratio being $a : b : c = 0·57243 : 1 : 0·54901$. The crystals are remarkable for the number of planes that they present. The mineral is colourless to white, and transparent. It has a hardness of 5·5 to 6, and a sp. gr. of 2·845.

An interesting feature is the presence of large numbers of liquid inclusions. In many of the cases, they are filled with water and liquid carbonic anhydride, and frequently also there is gaseous carbonic anhydride. Analysis gave the following results:—

P_2O_5.	BeO.	Na_2O.	Ignition.	Total.
55·86	19·84	23·64	0·08	99·42

It is thus evident that the mineral has the composition indicated by the formula $NaBePO_4$, a formula that is analogous to that of triphylite and lithiophilite. In form, the mineral seems to be related to herderite, the only other phosphate in which beryllium is known to exist. B. H. B.

Occurrence of Hanksite in California. By H. G. HANKS (*Amer. J. Sci.*, **37**, 63—66).—The author describes some magnificent crystals recently discovered at Borax Lake. He is of opinion that instead of being a rare mineral, hanksite will be found in great abundance, and will be proved to play an active part in the metamorphoses that produce gaylussite, thinolite, and perhaps borax. (Compare Abstr., 1886, 315). B. H. B.

Sperrylite, a New Mineral. By H. L. WELLS and S. L. PENFIELD (*Amer. J. Sci.*, **37**, 67—73).—This mineral is essentially an arsenide of platinum. It was found at the Vermilion mine, in the district of Algoma, Province of Ontario, Canada. The colour of the mineral is nearly tin-white, its hardness is between 6 and 7, and its sp. gr. is 10·602. Analysis gave the following results:—

As.	Sb.	Pt.	Rh.	Pd.	Fe.	SnO_2.	Total.
40·98	0·50	52·57	0·72	trace	0·07	4·62	99·46

The composition is consequently represented by the formula $PtAs_2$, a small portion of the platinum and arsenic being replaced respectively by rhodium and antimony. In composition, the mineral is nearer Wöhler's laurite, ($RuS_2 + \frac{1}{20}Ru_4O_5$), than any other mineral now known. It is possible that Wöhler's formula is slightly incorrect. The composition of the mineral corresponds with that of the artificial platinum arsenide made by Murray.

The crystalline form of sperrylite is shown by Penfield to be isometric. Simple cubes are common; octahedra are exceptional, whilst the majority of the crystals show combinations of the cube and octahedron. The mineral is named after F. L. Sperry, by whom the material for investigation was furnished. B. H. B.

Bertrandite from Pisek. By C. VRBA (*Zeit. Kryst. Min.*, **15**, 194—201).—On crystals of bertrandite from Pisek in Bohemia, the author has observed the following planes: $0P$, ∞P, $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $3\breve{P}\infty$, $2\breve{P}\infty$, $\infty\breve{P}3$, and $\frac{4}{9}\breve{P}\infty$; the last plane is new. The axial ratio is $a : b : c = 0·7191 : 1 : 0·4206$. The sp. gr. of the mineral was found to be 2·5986. Analysis gave the following results:—

SiO_2.	BeO.	H_2O.	Fe_2O_3.	Al_2O_3.	Total.
49·90	42·62	7·94	trace	trace	100·46

The formula therefore is $H_2Be_4Si_2O_9$. The analytical results are in accord with those obtained by Penfield (this vol., p, 24) in his examination of bertrandite from Colorado. B. H. B.

Composition of Tourmalin. By P. JANNASCH and G. CALB (*Ber.*, **22**, 216—221).—The analyses of the following samples of tourmalin are given below: I. Tourmalin from Snarum (black, sp. gr. at 22° = 3·134). II. Alabaschka (black, dark blue in thin layers, sp. gr. at 22° = 3·138). III. Piedra blanca (black, sp. gr. at 23° = 3·173). IV. Tamatawe (black, sp. gr. at 20·5° = 3·195). V. Mursinsk (black, sp. gr. at 20° = 3·210). VI. Ohlapian (black, sp. gr. at 25·3° = 3·084). VII. Buchworth (Australian, black, sp. gr. at 23·5° = 3·173). VIII. Barrado Perahy (Brazilian, green, sp. gr. at 23° = 3·029). IX. Brazilian (green):—

	SiO_2.	B_2O_3.	TiO_2.	F.	Al_2O_3.	Fe_2O_3.	FeO.
I.	35·64	9·93	1·10	—	29·41	2·90	6·56
II.	35·41	10·14	—	0·28	33·75	—	13·42
III.	34·73	9·64	0·30	0·47	31·69	3·18	10·14
IV.	35·48	9·49	1·22	0·33	25·83	6·68	7·99
V.	34·88	8·94	0·27	0·51	34·58	—	14·40
VI.	35·69	9·84	0·86	—	30·79	3·65	5·46
VII.	35·50	8·34	—	0·77	34·39	—	14·26
VIII.	37·40	10·74	—	0·98	39·02	—	2·35
IX.	37·05	9 09	—	1·15	40·03	—	2·36

	MnO.	CaO.	MgO.	Li_2O.	K_2O.	Na_2O.	H_2O.
I.	trace	1·56	8·00	—	0·16	3·03	2·94
II.	trace	0·17	1·57	—	0·34	2·08	3·41
III.	0·16	0·36	3·47	—	0·15	2·85	3·44
IV.	trace	2·03	6·90	—	0·29	1·92	2·58
V.	0·24	0·20	1·32	—	0·05	2·70	2·87
VI.	trace	1·54	8·12	—	0·27	2·53	3·20
VII.	trace	trace	0·51	—	trace	3·43	3·34
VIII.	2·57	0·60	0·20	1·33	0·29	3·59	3·08
IX.	2·35	0·47	0·32	0·60	trace	3·18	3 23

From these analyses, the author deduces the general formula $R_9BO_2(SiO_4)_2$. A. J. G.

Minerals of the Pacific Coast. By W. LINDGREN (*Zeit. Kryst. Min.*, **15**, 333—334, from *Proc. California Acad. Sci.*, 1887).—A variety of chlorite, similar to koschubeite, occurs with chromite in the serpentine of the Green Valley in the American River cañon. It is of a blood-red colour, and is found in crusts of small, thin, hexagonal tablets, as well as in compact masses with a finely fibrous structure and a pale purple colour. Its hardness is 2, and sp. gr. 2·69. On analysis, it gave the following results:—

SiO_2.	Cr_2O_3.	Al_2O_3.	FeO.	NiO.	MgO.	CaO.	H_2O.	Total.
31·74	11·39	6·74	1·23	0·49	35·18	0·18	13·04	99·99

These figures prove the mineral to be similar to koschubeite. The high percentage of chromium is remarkable. Optically, the mineral is positive, with an axial angle of about 3°. Associated with this mineral is an emerald-green garnet in small dodecahedra exhibiting distinct double refraction. B. H. B.

New Mineral from Franklin, New Jersey. By G. A. König (*Zeit. Kryst. Min.*, **15**, 334, from *Proc. Acad. Nat. Sci. Philadelphia*, 1887, 310—311).—This new mineral, named *bementite* after C. S. Bement, forms pale greyish-yellow masses resembling pyrophyllite. Its sp. gr. is 2·981. Analysis gave the following results:—

SiO_2.	MnO.	FeO.	ZnO.	MgO.	H_2O.	Total.
39·00	42·12	(3·75)	2·86	3·83	8·44	100·00

B. H. B.

Spessartine. By W. C. Robinson (*Journ. Anal. Chem.*, **1**, 251).—The author has analysed two varieties of spessartine with the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	Total.	Sp. gr.
I.	38·24	19·62	2·27	13·60	25·30	0·53	99·56	4·23
II.	40·92	9·24	1·13	9·28	38·34	trace	99·01	4·12

I. From Fairmount Park, Philadelphia; II. From Avondale, Pennsylvania. B. H. B.

Iron Ores of the Penokee-Gogebic Series of Michigan and Wisconsin. By C. R. Van Hise (*Amer. J. Sci.*, **37**, 32—48).—The author describes at length the character of the iron ores, the shape of the deposits, their relation to the rocks surrounding them, the nature of the rocks of the iron formation above the ore horizon, and the character of the formation above and below bearing iron. The shape of the deposits and their relations to the strata of the iron-bearing formation are such as to exclude the idea of original sedimentation in place, and they cannot be considered as the result of oxidation of iron carbonate in place alone. It is, however, certain that the iron carbonates formed the source whence the iron oxides for the ores were derived. The ores are thus necessarily concentrations of iron oxide, combined, perhaps, with iron oxide furnished by oxidation of carbonate in place. These conclusions accord with those of S. F. Emmons as to the origin of the silver-lead deposits of Leadville, Colorado. He finds that the ore did not form in pre-existing cavities, but by a gradual displacement of the rock materials by substances brought in solutions, and that these solutions did not come from below but from above. A like origin is more common among ore-deposits than has been believed. B. H. B.

Rocks of Pigeon Point, Minnesota. By W. S. Bayley (*Amer. J. Sci.*, **37**, 54—63).—At Pigeon Point, a bright red rock occurs along the borders of a large mass of olivine gabbro that forms the main portion of the point. Similar rocks have been observed at various places in the Lake Superior region, but no careful study has been made of them. The author shows that this red rock is not an altered gabbro nor an altered sedimentary rock as hitherto thought, but is the result of the solidification of a magma, which, under certain conditions, gave rise to a rock with the characteristics of a granophyre. The various phases of the red rock possess the same mineralogical composition and present gradation in structure from the granular (analysis I) to the porphyritic (analysis II) with granophyric ground-mass.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	BaO.	MgO.
I.	72·42	0·40	13·04	0·68	2·49	0·09	0·66	0·15	0·58
II.	74·00	0·34	12·04	0·78	2·61	0·05	0·85	0·12	0·42

	K_2O.	Na_2O.	H_2O.	P_2O_5.	Cl.	Total.	Sp. gr.
I.	4·97	3·44	1·21	0·20	trace	100·33*	2·620
II.	4·33	3·47	0·86	0·06	trace	99·93	2·565

The two rocks are obviously parts of the same mass. They both contain a sodium potassium felspar, and thus should be classed among the quartz-keratophyres. Upon the contact of the quartz-keratophyres with an olivine-gabbro, is a series of rocks having a composition intermediate between that of the keratophyre and that of the gabbro. These may be regarded as the results of contact action at great depths.

B. H. B.

Relation between Solfataras and Acidic Eruptive Rocks.

By A. de Lapparent (*Compt. rend.*, **108**, 149—151).—Solfataras are most abundant in volcanic districts which are characterised by the occurrence of acidic eruptive rocks in considerable masses. They are rare in the Sandwich Islands and in the neighbourhood of Vesuvius and Etna, where the rocks are mainly basic, but abound in the Chilian Andes, California, the district of the Yellowstone River, Java, and New Zealand, where the rocks are acidic.

There are no traces of solfataras in the Eifel and very few in Auvergne, but in Transylvania the solfataras which gave rise to the metalliferous deposits were formed in the midst of andesite, rhyolite, and other acidic rocks.

The solfataras seem to result from the gradual evolution of gases which were at one time incorporated with the lavas and are now being given off. Acidic rocks are very refractory, and by reason of their imperfect fluidity would retain to a very great extent the gases by which they were permeated at the time of eruption, and to which, as a matter of fact, their mobility is usually due. The presence of these gases in the lavas will retard the formation of crystals, and hence promote the growth of the large crystals which characterise this class of rocks.

C. H. B.

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* 100·37 in original.

Organic Chemistry.

Soluble Prussian Blue. By C. E. Guignet (*Compt. rend.*, **108**, 178—181).—Ordinary soluble prussian blue is a compound of prussian blue with potassium ferrocyanide. It is easily obtained by gradually adding to a boiling solution of 110 grams of potassium ferricyanide a hot solution of 70 parts of crystallised ferrous sulphate. The mixture is boiled for two hours, filtered, and the precipitate washed until the washings become dark blue. It is then dried at 100°, and has a fine deep-blue tint, and is very soluble in water. Admixed potassium ferrocyanide can be removed by washing with alcohol of 40 per cent. The compound is precipitated from its solution by sodium sulphate, sodium chloride, &c., but when the salts are removed by washing it redissolves. With salts of lead, zinc, and other metals, it yields, as Wyrouboff observed, a series of well-defined blue compounds.

Colloidal prussian blue was obtained by Graham by dialysis. Pure soluble prussian blue is obtained by suspending purified prussian blue in a saturated solution of oxalic acid, filtering, and allowing the mixture to remain for two months. Prussian blue is completely precipitated, and the liquid is quite colourless. After thorough washing with dilute alcohol, the precipitate is readily soluble in pure water. The same result is obtained in a very short time by precipitating the oxalic acid solution with strong alcohol or by a concentrated solution of sodium sulphate, and washing the precipitate with dilute alcohol. Ammonium oxalate or tartrate can be used instead of oxalic acid.

If the oxalic acid solution is boiled, insoluble prussian blue is precipitated, a result due to the action of the acid and not to the rise of temperature. Dilute sulphuric acid has the same effect at the ordinary temperature, and the precipitate does not dissolve even after long washing. The soluble and insoluble modifications have the same composition.

When prussian blue is heated with water and molybdic anhydride, it yields a deep-blue solution which is not affected by boiling or by gelatin. It is precipitated by sulphuric or nitric acid, but if the precipitate, which retains a small quantity of molybdic anhydride, is well washed with dilute alcohol, it dissolves in pure water. Ammonium molybdate and tungstate will also dissolve prussian blue.

When prussian blue is treated with concentrated sulphuric acid, it yields a soft, white mass like starch-paste, and if the temperature rises is partially decomposed. Hydroferrocyanic acid is liberated and partially dissolves in the excess of sulphuric acid. If the liquid is filtered through glass-wool and the filtrate cooled, it deposits the acid in long needles. The same result is obtained with lead or copper ferrocyanide.

If prussian blue which has been treated with sulphuric acid, is treated with absolute alcohol, it re-acquires its blue colour and dissolves in the alcohol. The same solution is obtained by dissolving solid prussian blue in a mixture of equal volumes of sulphuric acid and alcohol. When mixed with water or with a large excess of strong alcohol, the solution yields a precipitate of ordinary prussian blue, which retains sulphuric acid even after prolonged washing with dilute alcohol. Ethyl hydrogen sulphate does not dissolve prussian blue, and hence the phenomena just described cannot be attributed to the formation of this compound. C. H. B.

Relative Stability of the Alkyl Bromides. By F. LENGFELD (*Amer. Chem. J.*, **71**, 40—66).—The stability of alkyl bromides when in solution with various reagents has been determined.

With sodium hydroxide, potassium hydroxide, and ammonia, the relative stability is (in order of increasing stability), ethyl, propyl, butyl, isoamyl, isobutyl, isopropyl.

With nitric and sulphuric acids, the order of increasing stability is isopropyl, ethyl, propyl and butyl (about equal), isoamyl, isobutyl, ethylene.

With argentic nitrate and argentic nitrate and nitric acid, the order of increasing stability is isopropyl, ethyl, propyl, isoamyl, isobutyl, ethylene.

Experiments carried out on the influence of light on the stability of alkyl bromides in contact with sodium hydroxide showed that it was without influence on the result.

With dilute sodium hydroxide, *n*/40 and less, the velocity of changes is inversely as the concentration.

The action of sodium hydroxide on the bromides dissolved in methyl alcohol is slower than in propyl alcohol, and slower in propyl than in ethyl alcohol.

In the case of excess of one reagent over another, similar effects are produced by similar excess of ether reagent. J. W. L.

Analyses of Pure Sherry. By E. BORGMANN and W. FRESENIUS (*Zeit. anal. Chem.*, **28**, 71—77).—The authors, having obtained 18 samples of genuine sherry of various qualities, have analysed them by recognised methods and give the results in a table. The chief feature worthy of notice is the high percentage of sulphates. The universal practice of plastering the must for the manufacture of sherry renders it necessary to adopt for that wine an admissible maximum different from that allowed in unplastered wines. The sulphates found (calculated as potassium sulphate) ranged from 2·5—8·8 grams per litre. The superior brands (with two exceptions) contained more than 4 grams, and the inferior (with one exception) less than 3 grams per litre. The maximum limit of 3 grams proposed by the German Imperial Commission would exclude the finer wines of this class. Plastering increases the proportion of potassium in the wine, but not that of calcium. Phosphoric acid, chlorine, and magnesium appear to rise with increasing sulphates. In most of the samples, a deposition of tartar occurred on keeping. This fact is of interest in connection with the dictum of Blitz, that in judging of a wine containing much sulphates, it is necessary to consider whether at the same time a sufficient amount of hydrogen potassium tartrate is present.

M. J. S.

Boiling Points of Secondary Alcohols with Secondary Radicles: Diisopropyl Carbinol. By G. POLETEÉFF (*J. Russ. Chem. Soc.*, **20**, 672—686).—The author finds that the boiling point of diisopropyl carbinol, as given by Münch (*Annalen*, 180, 331), that is, 131·5°, does not agree with Flavitzky's (*J. Russ. Chem. Soc.*, 1871, 815, and 1887, 369) method of calculating boiling points, and that a higher number might be expected. He very carefully prepared the pure carbinol and determined its physical constants and those of other compounds formed during its preparation. The calcium salt of isobutyric acid was subjected to dry distillation, and *diisopropyl ketone*, $C_7H_{14}O$, was obtained. Its (corrected) boiling point was found to be 123·7°, the sp. gr. = 0·8230 at 0° and 0·8063 at 20° (water at 4° = 1). The molecular refractive power = 55·03—55·24 (calculated 55·37), or for infinite wave-length = 33·46 (calculated 33·58). On reduction with sodium amalgam of 3 per cent., it yields *diisopropyl carbinol*, $C_7H_{16}O$, boiling at 140° (corr.), having the sp. gr. 0·8445 at 0° and 0·8288 at 20°, and the molecular refractive power = 57·64 (calculated 57·37), or for infinite wave-length = 34·82 (calculated 34·89). The *acetate* boils at 160° (corr.), and has the sp. gr. 0·8856 at 0° and 0·8676 at 20·5°. From this, after hydrolysis, the original alcohol was obtained boiling at 140·4°. On oxidation with chromic mixture, the alcohol yields diisopropyl ketone, isobutyric acid, acetone, and some acetic acid (formed from the last). It is shown that the correct boiling point of diisopropyl carbinol, 140°, is in better accord with Flavitzky's theory than that obtained by Münch, namely, 131·5°. B. B.

Butyl Ethers. By E. REBOUL (*Compt. rend.*, **108**, 162—165; compare this vol., p. 366).—*Diisobutyl ether*, $O(CH_2{\cdot}CHMe_2)_2$, is readily obtained by the action of isobutyl bromide on the sodium-derivative of isobutyl alcohol. It is a mobile liquid only slightly soluble in water, and boils at 122—122·5° under a pressure of 760 mm.; sp. gr. at 15° = 0·7616. Concentrated hydrobromic acid converts it into isobutyl bromide boiling at 90—91°. The product of the action of isobutyl iodide on potassium isobutyl-oxide, which was believed to contain diisobutyl ether, is really a mixture of isodibutylene and isobutyl alcohol in nearly equivalent proportions.

Secondary isobutyl ether, $CHMe_2{\cdot}CH_2{\cdot}O{\cdot}CHMe{\cdot}CH_2Me$, is formed, together with isobutylene and the secondary alcohol, by the action of isobutyl bromide on the sodium-derivative of the secondary alcohol. It is insoluble in water and boils at 121—122; sp. gr. at 15° = 0·7652. Hydrobromic acid resolves it into isobutyl bromide and secondary butyl bromide.

Tertiary isobutyl ether cannot be obtained by the action of isobutyl bromide on the sodium-derivative of trimethyl carbinol, nor by the action of tertiary butyl bromide on sodium isobutyl oxide. *Disecondary butyl ether* is obtained in mere traces by the action of the secondary bromide on the sodium-derivative of the secondary alcohol, but the product consists mainly of the secondary alcohol and normal butylene. Secondary tertiary and ditertiary butyl ethers could not be obtained. C. H. B.

Oxidation of Glycerol. By E. Fischer and J. Tafel (*Ber.*, **22**, 106–110; compare Abstr., 1888, 1264).—*Trihydroxyisobutyric acid*, $OH\cdot C(CH_2\cdot OH)_2\cdot COOH$, is obtained when glycerose (250 grams) is mixed with anhydrous hydrocyanic acid (30 grams) and allowed to remain for 12 hours at 50° and a second 12 hours at 60° in a well-closed vessel. After the removal of the excess of hydrocyanic acid, the product is concentrated to 150 c.c., saturated with hydrogen chloride in a freezing mixture, and allowed to remain two days at the ordinary temperature. It crystallises from alcohol in slender, colourless prisms, melts at 116°, and is readily soluble in water, sparingly soluble in alcohol, and almost insoluble in ether, benzene, and chloroform. The *calcium* salt, with 4 mols. H_2O, crystallises in slender, matted needles; the *lead* salt, with 1 mol. H_2O, crystallises in slender, colourless prisms; the normal *barium* salt could not be crystallised; the basic *barium* salt, $C_4H_6O_5Ba$, is precipitated from a hot solution of the acid in slender needles; the *strontium* salt crystallises in slender needles; the *sodium* salt in prisms. On reduction with hydriodic acid and amorphous phosphorus in a reflux apparatus, trihydroxyisobutyric acid is converted into a mixture of acids containing iodine, and these, by further reduction with zinc-dust and dilute sulphuric acid, yield isobutyric acid.

Diiodoisobutyric acid, $C_4H_6O_2I_2$, can be extracted by ether from the product obtained on reducing trihydroxyisobutyric acid with hydriodic acid and amorphous phosphorus. It crystallises from water in long, colourless needles, melts at 127°, and is very readily soluble in alcohol and ether.

In addition to trihydroxyisobutyric acid, a small yield of erythroglucic acid is also obtained on treating glycerose with concentrated hydrocyanic acid. W. P. W.

Extraction of Sorbite. By C. Vincent and Delachanal (*Compt. rend.*, **108**, 147—148).—The fermented juice of *Sorbus aucuparia* is concentrated in a vacuum to one-third of its volume, and 10 grams are heated with excess of sulphuric acid, evaporated to dryness, the residue calcined, and the combined sulphuric acid estimated. The amount of sulphuric acid required to convert into sulphates all the bases in the juice is calculated from this result, and this quantity of acid is added to the concentrated juice, which is then diluted with its own volume of water and twice the volume of alcohol. The calcium and potassium, which interfere with the crystallisation of sorbite, are thus almost completely precipitated in the form of sulphates. The liquid is filtered, the alcohol distilled off, and the residue exactly neutralised with barium hydroxide, evaporated to a syrup, and extracted with boiling alcohol of 95°, which dissolves almost pure sorbite, and leaves in combination with the barium the viscous acid substances which usually interfere greatly with crystallisation. When the alcoholic solution is concentrated, it leaves a syrup which after a few days deposits a large quantity of sorbite in long needles.

Sorbite may be estimated in the form of dibenzoic acetal (following Abstract) in the following manner. The juice is concentrated in a vacuum to one-third its volume, mixed with excess of basic lead acetate, and the filtrate treated with hydrogen sulphide. The filtered liquid is concentrated in a vacuum to a thick syrup, mixed with its own weight of 50 per cent. sulphuric acid, and then with 80 per cent. of benzaldehyde. It rapidly becomes almost solid, owing to the formation of the acetal, which after 24 hours is thoroughly washed with water, dried, and weighed.

In order to separate sorbite from the acetal, the latter is heated with water which contains a few per cents. of sulphuric acid and benzaldehyde, and the liberated benzaldehyde is distilled off in a current of steam. The liquid is then treated with barium hydroxide to precipitate the sulphuric acid, and the barium present in the filtrate in the form of barium benzoate is exactly precipitated by addition of sulphuric acid. The liquid is then cooled, treated with ether in order to remove benzoic acid, and concentrated in a vacuum to a thick syrup, which after some days deposits crystals of sorbite.

C. H. B.

Dibenzoic Acetal of Sorbite. By J. MEUNIER (*Compt. rend.*, **108**, 148—149).—Sorbite when treated with benzaldehyde in presence of sulphuric or hydrochloric acid yields a dibenzoic acetal, $C_{20}H_{22}O_6$, which resembles the dibenzoic acetal of mannitol in constitution and properties. It is a white, confusedly crystalline substance, which melts at about 160°, is insoluble in water and almost insoluble in hot alcohol, but dissolves more readily in boiling benzene, chloroform, and acetic acid.

C. H. B.

Invert Sugar. By E. JUNGFLEISCH and L. GRIMBERT (*Compt. rend.*, **108**, 144—146; compare Abstr., 1888, 1266).—The rotatory power of pure levulose does not agree with that calculated for levulose from measurements with invert sugar, using Tuchschmid's and Tollens' formulæ, and assuming that invert sugar contains dextrose and levulose in equal molecular proportions. The rotatory power of pure levulose is not altered by admixture with pure glucose, and the authors find that the observed differences are due to the action on the levulose of the acids which are used to produce inversion.

The rotatory power of a 10 per cent. solution of pure levulose increases from $[\alpha]_D = -94° 66'$ to $-96° 78'$ when heated for half an hour at 68° with 5 per cent. of hydrochloric acid. With a similar quantity of sulphuric acid, under the same conditions, the rotatory power rises to $-99° 77'$. There is no sensible variation in the results when the liquid is neutralised before the measurements are made. The action of strong inorganic acids on levulose takes place at once at the ordinary temperature, oxalic acid behaves like the inorganic acids when heated, whilst formic and acetic acids of similar concentration do not affect the levulose. The rotatory power of glucose shows no variations of this kind.

The duration of the action of the acids used for inversion has long been known to affect the rotatory power of the product.

Comparative experiments with levulose and invert sugar under the conditions described show that the rotatory power of the levulose in the invert sugar, $[\alpha]_D = -96° 52'$, agrees with that of pure levulose which has been subjected to the same treatment, $[\alpha]_D = -96° 78'$. Clerget's method of inversion by treating with 10 per cent. of hydrochloric acid at 68° for 10 minutes, gives a levulose with a rotatory power of $[\alpha]_D = -101° 30'$, whilst pure levulose treated in the same way has a rotatory power of only $[\alpha]_D = -97° 44'$, which is practically the same as that obtained by treating levulose with hydrochloric acid in the cold.

That these differences are due to the action of the inorganic acids is shown by the fact that if sugar is inverted by treatment with 5 per cent. of acetic or formic acid at 100° for 30 minutes, the rotatory power remains constant even after prolonged heating, and the rotatory power of the levulose which the product contains is identical with that of pure levulose. Addition of hydrochloric acid to this product at once alters the rotatory power of the levulose.

It is evident that the levulose contained in invert sugar which has been prepared in the usual way is not identical with pure crystallised levulose, but is a product of the alteration of the latter by the action of the mineral acids employed. C. H. B.

Fermentation of Galactose, Arabinose, Sorbose, and other Sugars. By W. E. Stone and B. Tollens (*Annalen*, **249**, 257—272).—Most of the results obtained by the authors have already been published (Abstr., 1888, 808). With yeast supplied with suitable nourishment, galactose ferments as completely as dextrose, but less rapidly. Sorbose ferments more slowly and less completely. Arabinose and milk-sugar ferment very slowly and incompletely. Pure yeast does not bring about the fermentation of arabinose.

W. C. W.

Formation of Furfuraldehyde and Non-production of Levulinic Acid from Arabinose: Formation of Furfuraldehyde as a Test for Arabinose: Formation of Arabinose and Xylose from Malt Residues. By W. E. Stone and B. Tollens (*Annalen*, **249**, 227—245).—In addition to the results which have already been published (Abstr., 1888, 1060), the authors have obtained arabinose and xylose from the malt which has been used for brewing. Furfuraldehyde is formed when xylose is boiled with dilute acids.

W. C. W.

Mannose. By E. Fischer and J. Hirschberger (*Ber.*, **22**, 365—376).—The authors have simplified their method for the preparation of mannose (compare Abstr., 1888, 934) as follows:—Mannitol (3 kilos.) is heated at 40—45° with water (20 litres) and nitric acid of sp. gr. 1·41 (10 litres) with constant stirring. In four to five hours, evolution of gas commences, and, as soon as it is found that a small portion of the solution, after neutralising with sodium carbonate, gives a dense, yellowish precipitate with phenylhydrazine acetate, which is generally the case after five to six hours, the operation is brought to an end. The liquid is cooled to about 25° by throwing in ice, then made slightly alkaline with solid sodium carbonate to destroy the nitrous acid, and finally acidified with acetic acid. Phenylhydrazine (1 kilo.), dissolved in dilute acetic acid, is added to the solution, and after an hour's time the separated hydrazone is washed and pressed. About one-quarter of the product is boiled for about 15 minutes with water (5 litres), the filtered solution decolorised by heating with zinc-dust and ammonia, and again filtered; the hydrazone separates in pale yellow plates, and the mother-liquors are employed for recrystallising another portion of the crude product, this process being repeated six or seven times until the whole is purified. The yield of hydrazone is, on the average, 10 per cent. of the mannitol employed.

The pure hydrazone (100 grams) is dissolved in hydrochloric acid of sp. gr. 1·19 (400 grams), and, after keeping for half an hour, the solution is cooled in a freezing mixture, and the crystals separated by filtration. The filtrate is diluted with water (2 vols.), neutralised with lead carbonate, and filtered; the yellow solution is made alkaline with baryta, extracted with ether to remove phenylhydrazine and coloured products, then treated with carbonic anhydride, decolorised with animal charcoal, and concentrated to about 300 c.c. The residue is treated with sulphuric acid to precipitate the barium, neutralised with lead carbonate, filtered, evaporated in a partial vacuum, and again filtered. The filtrate is evaporated to a syrupy consistency, dissolved in absolute alcohol (5 vols.), treated with hydrogen sulphide, and, after separating the lead sulphide, the mannose is precipitated by adding a large volume of ether. It is thus obtained in the form of a colourless syrup containing about 90 per cent. of sugar. 100 grams of the hydrazone yield 60 grams of the syrup.

Mannose is precipitated in amorphous, white flocks when ether is added to an alcoholic solution of the syrup; on keeping under absolute alcohol, the precipitate solidifies to a hard, colourless mass which, however, shows no distinctly crystalline structure. It is hygroscopic, deliquescent, and very readily soluble in water, but very sparingly in boiling absolute alcohol, and insoluble in ether. It does not produce a coloration in the magenta and sulphurous anhydride solution. Alcoholic potash precipitates a flocculent, hygroscopic substance from alcoholic solutions of the sugar; lead acetate and ammonia produce in aqueous solutions a precipitate which becomes yellow on keeping, or when warmed. The specific rotatory power is $[\alpha]_D = 12·96$, and 1 c.c. of Fehling's solution corresponds with 4·307 milligrams of mannose. The quantity of mannose present in the solutions employed for the determination of the rotatory power and reducing power was estimated by means of the phenylhydrazone; as, however, this compound is not quite insoluble in water, there is a slight error in both determinations. Cane-sugar, maltose, raffinose, trehalose, various kinds of molasses, manna, potato-starch, lichenin, gum tragacanth, gum arabic, quince seeds, linseed, fleabane, and Carragheen moss were tested for mannose, but in no case could the presence of this sugar be detected. Salep juice, however, as previously stated by Tollens and Gans, on inverting, yields mannose which can be isolated by means of the hydrazone. The yield of hydrazone is 5 to 6 per cent. of the bulbs employed.

When a dilute solution of mannose is heated at 110° for about four hours, humous substances are formed, and on distilling the filtered solution it yields furfuraldehyde.

Levulinic acid is formed, together with humous substances, when mannose phenylhydrazone is heated with fuming hydrochloric acid.

When mannose (0·25 gram) is heated for three hours with 7·5 per cent. hydrochloric acid (32 c.c.), small quantities of humous substances are formed, but only 0·07 gram of the mannose is decomposed. (Compare Sieben, *Zeit. anal. Chem.*, **24**, 138.)

Mannose (50 grams) dissolved in water (250 grams) was mixed with anhydrous hydrogen cyanide (18 c.c.) and a few drops of ammonia, and kept in a closed vessel at the ordinary temperature; a flocculent substance soon separates, and after three days the reaction is brought to an end by warming at 50° for four hours. The flocculent product seems, from its behaviour towards alkalis and iron salts, to be the amide of mannosecarboxylic acid; it is insoluble in hot water, and, after decolorising with animal charcoal, alcohol precipitates from the solution a white, amorphous powder melting at 182—183° with decomposition. The filtrate from this amide contains considerable quantities of the ammonium salt of the acid.

Barium mannosecarboxylate, $(C_7H_{13}O_8)_2Ba$, is prepared by evaporating the crude product of the action of hydrogen cyanide on mannose until free from hydrogen cyanide, adding water and baryta (80 grams), and again evaporating until the evolution of ammonia ceases. The residue is dissolved in water (4 litres), carbonic anhydride passed through it, the solution decolorised with animal charcoal, and evaporated until the barium salt commences to separate; further small quantities can be obtained by mixing the mother-liquor with alcohol and ether. The yield is almost theoretical. It is a colourless, semicrystalline compound, and is moderately soluble in hot water, but only very sparingly in cold water, and insoluble in alcohol.

The *lactone*, $C_7H_{12}O_7$, is obtained when a hot, aqueous solution of the barium salt is decomposed with the requisite quantity of sulphuric acid. It crystallises in needles, melts at 148—150°, and is very readily soluble in water, but only moderately in absolute alcohol, and insoluble in ether.

A second product, probably *mannosecarboxylic acid*, was sometimes obtained in small quantities in preparing the lactone; this substance has an acid reaction, melts at 167—169° with evolution of gas, and is more readily soluble in alcohol than the lactone.

Heptylic acid (normal) is formed when barium mannosecarboxylate (35 grams) is boiled for five hours with hydriodic acid boiling at 127° (250 grams) and amorphous phosphorus (10 grams). The product is diluted with water, extracted with ether, and the extract shaken with mercury to remove iodine. The oil (27 grams) which is obtained on evaporation is treated in the cold with zinc-dust and dilute sulphuric acid to reduce the iodine-compounds, which are present in considerable quantities, and then distilled with steam. The distillate contains heptylic acid (= 7 grams barium salt) and a neutral oil (2 grams) probably heptolactone.

Mannose is readily oxidised by bromine in aqueous solution; the acid obtained seems to be different from gluconic acid. It is also oxidised by nitric acid, but the acid has not yet been investigated.

The compound described as phenylmannosazone (*loc. cit.*) is identical with phenylglucosazone.

From the authors' experiments, it follows that mannose is the aldehyde of mannitol, and has, therefore, the same constitution as dextrose, with which it is physically isomeric. Since the phenylhydrazones of mannose and dextrose are totally distinct substances, both of which are readily converted into one and the same osazone, $N_2HPh\cdot CH\cdot C(N_2HPh)\cdot [CH\cdot OH]_3\cdot CH_2\cdot OH$, it must be assumed that the isomerism of the two sugars is determined by the carbon-atom which is directly combined with the aldehyde-group. As dextrose has a much greater specific rotatory power than mannose, the former must be looked on as the dextro-, the latter as the lævo-modification of the same system. The compounds which these sugars form with hydrogen cyanide are isomeric, as, probably, are also the corresponding carboxylic acids; as both sugars yield one and the same compound on reduction, some change must occur in the arrangement in space of the $COH\cdot CH\cdot (OH)$-group. The difference in behaviour on reduction seems to show that mannose, in its physical as well as chemical structure, is the true aldehyde of mannitol, whilst dextrose is the aldehyde of a physically isomeric hexahydric alcohol. F. S. K.

Formation of Acrose from Formaldehyde. By E. Fischer and F. Passmore (*Ber.*, **22**, 359—361).—Formose (compare Löw, *J. pr. Chem.*, **33**, 321), as the authors have previously shown, is a mixture of various aldehyde- and ketone-alcohols, which can be separated by means of the osazones.

Pure α-acrosazone can be isolated as follows:—Formaldehyde (100 grams) in 3 per cent. aqueous solution is first treated as described by Löw, the solution is then neutralised with acetic acid, and warmed on the water-bath for four hours with a mixture of phenylhydrazine (100 grams) and 50 per cent. acetic acid (100 grams). The cold solution is filtered, and the residual mixture of osazones dried on porous plates, and then extracted several times, first with cold benzene, and then with ether, to remove resinous products and the more readily soluble osazones. The dirty yellow, crystalline residue (20 grams) is extracted with water (6 litres) to remove phenylformosazone, washed twice with cold, absolute alcohol (10 c.c.), and then boiled twice for a long time with alcohol (10 c.c.). α-Acrosazone (1·1 gram) remains as a yellowish-green powder, and cannot be purified by recrystallisation. It is therefore converted into the osone by warming for one minute at 45° with fuming hydrochloric acid; the cold solution is separated from the phenylhydrazine salt, diluted with water (5 vols.), neutralised with lead carbonate, and filtered. The filtrate is warmed with phenylhydrazine acetate, and the osazone which is formed is obtained pure by recrystallising from a large quantity of hot alcohol. The compound thus prepared has all the properties of α-acrosazone.

The fact that acrose is very nearly related to the naturally occurring saccharoses lends considerable probability to Baeyer's views concerning the formation of grape-sugar in the vegetable kingdom.

F. S. K.

Compounds of Phenylhydrazine with Sugars. By E. FISCHER (*Ber.*, **22**, 87—89; compare Abstr., 1888, 1267).—The author proposes "osone" as a general term for compounds of the type of oxyglucose, and throughout the paper refers to this compound as glucosone.

Glucosone reacts with methylphenylhydrazine in alcoholic solution in the cold, forming *glucosone methylphenylhydrazone*,

$$C_6H_{10}O_5:N{\cdot}NMePh,$$

which crystallises from water in slender, colourless scales, and melts at 171° when rapidly heated; with an excess of the hydrazine in acetic acid solution, however, *methylphenylglucosazone*, $C_{20}H_{26}N_4O_4$, is obtained, and this crystallises from benzene in slender, yellowish-red needles melting at 152° with decomposition. When treated in aqueous solution with solutions of orthodiamines free from acids, glucosone readily yields condensation compounds; thus, with orthotoluylenediamine, it forms *anhydroglucometaparadiamidotoluene*, $C_{13}H_{16}N_2O_4$, which crystallises in colourless, slender needles and melts at a few degrees above 180° with decomposition (compare Griess and Harrow, Abstr., 1887, 930).

Glucosone decomposes into a mixture of humous substances and furfuraldehyde when heated in dilute aqueous solution at 140° for several hours, and into humous substances, carbonic anhydride, and a small quantity of levulinic acid when heated with hydrochloric acid. It is readily reduced by means of zinc-dust and acetic acid at 100°, and is thereby converted into levulose.

Galactosone and *rhamnosone* have been prepared from galactose and rhamnose (isodulcitol) by methods similar to that adopted for the preparation of glucosone. W. P. W.

Synthetical Experiments in the Sugar-group. By E. FISCHER and J. TAFEL (*Ber.*, **22**, 97—101; compare Abstr., 1888, 358).—*α-Acrosone* is obtained when α-acrosazone is rapidly heated to 45° with 20 times its weight of fuming hydrochloric acid (sp. gr. = 1·19), maintained for one minute at this temperature until phenylhydrazine hydrochloride begins to crystallise out, then rapidly cooled to 25° and kept at this temperature for 5 to 10 minutes until the reaction is complete. The product is purified by the method employed in the case of glucosone (oxyglucose) (Abstr., 1888, 1267), and the yield amounts to about 50 per cent. of that theoretically possible. It is a colourless syrup, which solidifies in the cold to a hard, amorphous mass, and in dilute aqueous solution reacts with phenylhydrazine acetate in the cold, forming α-acrosazone. On treatment with orthotoluylenediamine, α-acrosone is converted into a compound, which crystallises in slender needles, becomes brown at 180° and melts at 185° with decomposition, thus closely resembling anhydroglucometaparadiamidotoluene (compare preceding Abstract). When heated in aqueous solution for several hours at 140°, α-acrosone decomposes into humous substances and furfuraldehyde, and when heated with 18 per cent. hydrochloric acid at 100° for six hours it decomposes into humous substances and a small quantity (2½ per cent.) of levulinic acid.

α-Acrose, $C_6H_{12}O_6$, is formed by heating α-acrosone in dilute aqueous solution at 100° with zinc-dust and acetic acid. When the reduction is complete, the solution is freed from zinc by means of hydrogen sulphide, evaporated to dryness in a vacuum, and the residue extracted with absolute alcohol, the concentrated alcoholic solution being finally precipitated by ether. α-Acrose is a sweet syrup which reduces Fehling's solution, yields α-acrosazone on treatment with phenylhydrazine acetate at 100°, and is fermentable by yeast. On reduction with sodium amalgam, it is converted into *acritol*, $C_6H_{14}O_6$, which crystallises in spherical aggregates of thin plates, melts at 164—165°, has a sweet taste, does not reduce alkaline copper solution, is readily soluble in water, very sparingly soluble in alcohol, and, in short, differs only from mannitol in being optically inactive. W. P. W.

Rhamnodiazine. By B. Raýmann and K. Chodoůnský (*Ber.*, **22**, 304—305).—Rhamnodiazine, $C_{18}H_{32}O_8N_2$, is formed when rhamnose is treated with ammonia and ethyl acetoacetate (2 mols.) at the ordinary temperature in methyl alcohol solution. It separates after a few days in long, soft needles, and is purified by recrystallising first from alcohol and then from hot water. It melts at 186° and is decomposed when heated more strongly; it is soluble in alcohol and hot water, but only sparingly so in chloroform, and insoluble in ether, light petroleum, and carbon bisulphide. It dissolves in large quantities in glacial acetic acid, with which it probably combines; the compound is, however, unstable, as rhamnose crystallises from the solution after a short time. It reduces Fehling's solution and a neutral solution of silver nitrate very readily, but ammoniacal silver nitrate solution is only very slightly acted on.

Other glucoses seem to yield similar compounds when treated with ethyl acetoacetate or ketones and ammonia as described above; these substances are not easily obtained in crystals. F. S. K.

Oxidation of Milk-sugar. By E. Fischer and J. Meyer (*Ber.*, **22**, 361—364).—*Lactobionic acid*, $C_{12}H_{22}O_{12}$, is obtained when milk-sugar (1 part) dissolved in water (7 parts) is treated with bromine (1 part) at the ordinary temperature, the mixture being frequently shaken. The bromine dissolves in the course of one to two days and, after keeping for another 48 hours, a stream of air is passed through the solution to drive off most of the free bromine, the remainder being converted into hydrobromic acid by passing hydrogen sulphide into the cooled solution. The quantity of hydrobromic acid present having been ascertained by titrating a portion of the solution with silver nitrate, the calculated quantity of lead carbonate is added, and the hydrobromic acid remaining in the filtered solution is carefully precipitated with silver oxide. The solution is filtered, treated with hydrogen sulphide, and the filtrate evaporated. The acid, syrupy liquid thus obtained is agitated for a long time with large quantities of cold glacial acetic acid to remove reducing substances and other products, the colourless residue, the weight of which is about one-third that of the lactose employed, is dissolved in water and the warm solution precipitated with a hot, concentrated solution of basic lead acetate. The solution of basic lead acetate is prepared by dissolving the neutral salt (2 parts) and lead hydroxide (1 part) in hot water (3 parts) and dissolving the crystals, which separate on cooling, in pure, hot water. The precipitated lead salt is quickly separated by filtration, washed with hot water, and then suspended in cold water and decomposed with hydrogen sulphide. The filtrate is evaporated on a water-bath in a partial vacuum, the residue treated with alcohol and ether to remove acetic acid, and finally dissolved in a small quantity of water and reprecipitated with alcohol and ether.

Lactobionic acid is a colourless, strongly acid syrup, and is very readily soluble in water but only very sparingly in alcohol and cold glacial acetic acid, and is insoluble in ether. It decomposes carbonates, but does not reduce Fehling's solution even on boiling. The *calcium*, $(C_{12}H_{21}O_{12})_2Ca$, *barium*, $(C_{12}H_{21}O_{12})_2Ba$, *cadmium*, and *lead* salts were prepared by warming an aqueous solution of the acid with the corresponding carbonate; they are all insoluble in alcohol, but readily soluble in water excepting the basic lead salt. On evaporating the aqueous solution over sulphuric acid, the salts are obtained in the form of syrups which gradually solidify but do not clearly show a crystalline structure.

Lactobionic acid is decomposed into galactose and gluconic acid when warmed with dilute mineral acids. The pure acid was heated at 100° for an hour with 5 per cent. sulphuric acid; the gluconic acid was then isolated by means of the barium salt, and identified by converting it into the calcium salt (Kiliani, *Annalen*, **205**, 184). The filtrate was evaporated, and the galactose, which crystallised from the solution, identified by converting into the osazone.

The formation and decomposition of lactobionic acid confirm Fischer's conclusions (Abstr., 1888, 1267) with regard to the constitution of milk-sugar.

An acid, isomeric with lactobionic acid, can most probably be obtained from maltose by the process described above; this compound, on inverting, should yield gluconic acid and dextrose. F. S. K.

Derivatives of Trimethylenediamine. By S. Gabriel (*Ber.*, **22**, 224—226).—β-Hydroxytrimethylenediphthalimide (Goedeckemeyer, Abstr., 1888, 1294) is best prepared by heating an intimate mixture of α-dichlorhydrin (13 grams) and potassium phthalimide (37 grams) at 140—150°; as soon as the reaction commences, the mixture is cooled to about 100° and finally heated at about 160—180° for half an hour. The crude product is recrystallised from acetic acid, and washed first with dilute alcohol and then with water. The yield is 50 per cent. of the theoretical quantity. When β-hydroxytrimethylenediphthalimide is heated at 200° with concentrated hydrochloric acid, it yields hydroxytrimethylenediamine hydrochloride, and when treated in like manner with hydrobromic acid of sp. gr. 1·49, it is converted into the corresponding hydrobromide.

β-Bromotrimethylenediamine hydrobromide, $CHBr(CH_2{\cdot}NH_2)_2,2HBr$, is obtained when the preceding compound (15 grams) is heated for four hours at 200—210° with hydrobromic acid (45 c.c.) saturated at 0°; the product is dissolved in cold water, the filtered solution

evaporated to dryness, and the residue recrystallised from dilute alcohol. It crystallises in plates, decomposes at 210—215°, and is readily soluble in water but sparingly so or insoluble in absolute alcohol. The *picrate*, $C_3H_9BrN_2,2C_6H_3N_3O_7$, melts at 215—217° with previous softening, and is soluble in hot water. The *aurochloride*, $C_3H_9BrN_2,2HAuCl_4$, crystallises in plates. The *platinochloride*, $C_3H_9BrN_2,H_2PtCl_6$, crystallises in orange-yellow plates. The *ferrocyanide*, $(C_3H_9BrN_2)_2,H_4Fe(CN)_6$, is a colourless, granular, crystalline salt.
F. S. K.

Action of Sulphurous Anhydride on Tiglic Aldehyde. By F. H. HAYMANN (*Monatsh.*, **9**, 1055—1066; compare Abstr., 1883, 570, and this vol., p. 121).—Excess of sulphurous anhydride was passed into water (50 c.c.) containing tiglic aldehyde (5 grams); the mixture being kept cool by means of ice. The saturated solution was placed in a closely stoppered bottle, well shaken and allowed to remain for three hours at the ordinary temperature, when the solution was neutralised in the cold with barium carbonate; on concentration in a vacuum at a temperature not above 35°, a quantity of barium sulphite separated, and on further concentration, a gummy mass remained, which consisted of a mixture of barium hydroxypentanedisulphonate and barium valeraldehydesulphonate. When the saturated solution was heated in sealed tubes for four hours at 65°, and then treated in a way similar to that above mentioned, the same results were obtained. Hydroxypentanedisulphonate was, however, completely converted into the mono-acid when heated at 100°.

On reduction with sodium amalgam in a solution always containing a small quantity of uncombined sulphuric acid, both valeraldehydesulphonic acid and hydroxypentanedisulphonic acid gave hydroxypentanesulphonic acid, $SO_3H{\cdot}CMeEt{\cdot}CH_2{\cdot}OH$, the latter with formation of sulphurous anhydride. On heating with lime, sodium hydroxypentanesulphonate yielded a mixture of tiglyl alcohol and methylethylcarbin carbinol, $CHMeEt{\cdot}CH_2{\cdot}OH$; whilst sulphovaleric acid was formed on oxidation with bromine-water.
G. T. M.

Metacetone. By E. FISCHER and W. J. LAYCOCK (*Ber.*, **22**, 101—105).—By distilling sugar with lime, Fremy obtained a compound boiling at 84°, which he termed metacetone, and to which he ascribed the formula $C_6H_{10}O$. An examination of the products obtained by distilling sugar with lime under the conditions described by Gottlieb (*Annalen*, **52**, 127) shows that metacetone does not exist, and that Fremy's substance is a mixture of propaldehyde, dimethylfurfuran, and a third hydrocarbon-like compound.

When sugar is distilled with three times its weight of lime, a distillate is obtained which separates into an aqueous and an oily layer. The aqueous layer contains much acetone. The oily layer can be separated into two fractions boiling at 30—115° and 115—280° respectively. The compounds contained in the first fraction were recognised by the hydrazones obtained by treating it with phenylhydrazine, and they comprised acetone, hydrocarbons, and further propaldehyde, dimethylfurfuran, and probably higher and lower homologues of these.

An examination of the "light oil" from wood-tar shows that propaldehyde and dimethylfurfuran are present. W. P. W.

Chlorocrotonic Acids. By A. KOLL (*Annalen*, **249**, 303—326). —By the action of phosphorus pentachloride on the ethylic salt of methylacetoacetic acid, Isbert (Abstr., 1886, 1010) obtained a mixture of ethyl mono- and di-chloromethylacetoacetates and α-methyl-β-chlorotetracrylic acid. The author finds that the yield of acid is considerably increased by adding the ethyl salt of methylacetoacetic acid to an excess of phosphorus pentachloride, warming the mixture at 70°, and when cold, pouring the product into water. *Methyl α-methyl-β-chlorotetracrylate* is a mobile liquid boiling at 158·5° (corr.), sp. gr. 1·131 at 15°. The ethyl, propyl, and isobutyl salts boil respectively at 171—172°, 189—190°, and 201—202°. The copper salt is not crystalline. The ethyl salt is decomposed by a strong solution of potassium hydroxide, yielding alcohol and ethyl methyl ketone. Methyl α-methyl-β-chlorotetracrylate is acted on by sodium ethoxide and propoxide, yielding the *methyl α-methyl-β-ethoxytetracrylate* and *methyl α-methyl-β-propoxytetracrylate* respectively. The former boils at 203—204° and the latter at 215—216°.

α-Ethyl-β-chlorotetracrylic acid is freely soluble in alcohol and ether. It crystallises in colourless needles, melts at 49·5° and boils at 215°. The *methyl* salt boils at 166—167°, sp. gr. 1·087 at 15°. The *ethyl* salt boils at 182—183°, the *propyl* salt at 197—198°, and the *isobutyl* salt at 207—208°. The *zinc* salt, $(C_6H_8ClO_2)_2Zn + 1\frac{1}{2}H_2O$, forms needles, and the magnesium salt, $(C_6H_8ClO_2)_2Mg + 2H_2O$, crystallises in plates. The copper salt is an insoluble amorphous powder. The potassium salt is decomposed by potassium hydroxide at 150°, forming methyl propyl ketone. Sodium methoxide and ethoxide act on the methylic salt of ethylchlorotetracrylic acid, forming the methyl salts of α-ethyl-β-methoxy-, and α-ethyl-β-ethoxy-tetracrylic acids boiling at 188—190° and 208—209° respectively.

The preparation of β-chloroquartenylic acid has been described by Genther and Frölich. The ethyl salt boils at 155—156°. It is converted into *ethyl β-ethoxyquartenylate*, $CH_2{:}C(OEt){\cdot}CH_2{\cdot}COOEt$, by the action of sodium ethoxide. This compound readily crystallises in rhombic plates. It melts at 29·5° and boils at 191—192°.

W. C. W.

Ketosulphides and Ketosulphide-acids. By A. DELISLE (*Ber.*, **22**, 306—309).—The compound obtained by treating ethyl acetoacetate with sulphur dichloride (compare Abstr., 1887, 915) has the composition $C_{12}H_{18}O_6S$, and is identical with the substance prepared by Buchka (Abstr., 1885, 1200) from ethyl sodacetoacetate and sulphur monochloride. It separates from benzene in well-defined crystals melting at 83—84°, but after recrystallising from alcohol it has no well-defined melting point. When treated with reducing agents, hydrogen sulphide is evolved, so that the constitution of this compound is probably $S(O{\cdot}CMe{:}CH{\cdot}COOEt)_2$.

Acetonylphenyl sulphide, $C_9H_{10}OS$, is obtained by gradually adding the calculated quantity of chloracetone to a well-cooled mixture of ether and sodium thiophenoxide (NaSPh), the whole being constantly shaken. It separates from ether in large, well-defined crystals, melts at 34—35°, boils at about 143—145° (15 mm.), and is moderately soluble in alcohol, but only sparingly in light petroleum. It dissolves in concentrated sulphuric acid with a yellowish-red coloration, which turns dark-violet on warming. The *hydrazone* melts at 82—83°.

Phenylacetonylphenylsulphide, $C_{14}H_{12}OS$, prepared in like manner from bromacetophenone and sodium thiophenoxide, crystallises from alcohol in colourless needles or plates, melts at 52—53°, and is very readily soluble in ether and acetone.

Ethyl β-thiophenyllevulinate, $C_{13}H_{16}O_3S$, can be obtained from sodium thiophenoxide and ethyl bromolevulinate as described above; it is a liquid boiling at 196—197° (15 mm.). F. S. K.

Molecular Weight of Pentic Acid. By R. Moscheles and H. Cornelius (*Ber.*, **22**, 243—244; compare Abstr., 1888, 1272).—Determinations of molecular weight by Raoult's method made with ethyl pentate in glacial acetic acid solution gave the numbers: 153, 155, and 158, and thus confirm the formula $OEt{\cdot}C\left<\begin{matrix}CEt{\cdot}CO\\CH_2{-}O\end{matrix}\right>$.

N. H. M.

Ketonic Acids. By J. Seissl (*Annalen*, **249**, 272—303).—*Chlorolevulinic acid*, $C_5H_7ClO_3$, is the product of the action of phosphorus pentachloride on levulinic acid. It is a pale-yellow oil which cannot be distilled. No salts of the chlorinated acid could be obtained by neutralising the acid with bases or carbonates. Chlorine converts levulinic acid into *dichlorolevulinic acid*, $C_5H_6Cl_2O_3$; this is crystalline and melts at 77°. When phosphorus pentachloride acts on ethyl levulinate, a mixture of the ethyl salts of mono- and di-chlorolevulinic acids is formed.

Pyruvic acid is less readily attacked by chlorine at the ordinary temperature than levulinic acid. A mixture of the ethyl salts of mono- and di-chloropyruvic acids is formed by the action of phosphorus pentachloride on pyruvic acid. Under similar treatment, ethyl pyruvate appears to yield a mixture of ethyl tri- and tetra-chloropropionates. W. C. W.

Potassium Antimony Oxalate. By R. Wagner (*Chem. Zeit.*, **12**, 1726).—The crystals of potassium antimony oxalate resemble in form those of oxalic acid; it gives a clear solution with small quantities of hot water, but with much water it is partially decomposed, a basic antimony salt being deposited, whilst an acid salt remains in solution. The finely powdered salt loses 2·5 mols. H_2O at 75°, the rest of its water is given off at 130°, above which temperature further decomposition ensues.

Commercial crystalline potassium antimony oxalate has the composition $Sb_2(C_2O_4)_3 + 3K_2C_2O_4 + 8H_2O$; the salt prepared by Souchay and Lenssen's method has the same composition.

The antimony was estimated both volumetrically and gravimetrically. In the former case, excess of $\frac{N}{10}$ iodine solution was added to the neutral or feeble acid antimony solution, and titrated back with thiosulphate. Acid stannous solutions can be titrated in the same way under certain conditions. D. A. L.

Symmetrical Dimethylsuccinic Acids. By C. A. Bischoff and E. Voit (*Ber.*, 22, 389—391; compare Abstr., 1888, 254 and 1057).—Antidimethylsuccinic acid (m. p. 120°) is obtained, together with the isomeric acid, by hydrolysing ethyl dimethylethenyltricarboxylate, and the two products can be separated by recrystallising from water. Its solubility in water at 14° is 1 : 33·3, that of the para-acid 1 : 97. It is directly converted into pure pyrocinchonic acid when treated with bromine at 130°. The *ethyl* salt is a colourless oil, boils at 221—222°, and is decomposed into ether and the anhydride when heated at a high temperature. The *calcium* salt crystallises with 2 mols. H_2O and is insoluble in cold water. The *silver* salt is anhydrous and unstable. The anhydride, obtained by heating the acid at 200°, melts at 87°, and yields only the anti-acid when treated with water. It is converted into pyrocinchonic acid when heated at 90° with bromine in chloroform solution. The *imide* melts at 106°, and yields only the anti-acid when treated with potash. The *anil* crystallises from hot alcohol in small needles and melts at 146°. The *dianilide*, prepared by treating the chloride with aniline, crystallises from alcohol in colourless needles melting at 222°. It yields the anti-acid only when decomposed with potash.

When paradimethylsuccinic acid is heated at 180—196°, it yields an anhydride which melts at 87°, and is very similar to that obtained from the anti-acid. This anhydride yields a mixture of both acids, the relative quantities of which vary with the length of time during which the original para-acid was heated. When the para-acid is treated with acetic chloride, it gives an *anhydride* melting at 38°, from which only the original acid is obtained.

When the para-acid is heated with ammonia, it yields a mixture of imides which gives the anti-acid together with small quantities of the para-compound. The *imide* prepared by heating the para-ethyl salt with ammonia, crystallises from benzene, melts at 78°, and yields only the para-acid. An anil, melting at 126°, was obtained; it gives about equal quantities of the two acids when treated with alcoholic potash. The *anilide* melts at 235°, and is very similar to the anilide of the anti-acid; it yields only the para-acid when decomposed with alcoholic potash.

The para-acid yields pyrocinchonic acid when treated with bromine. No unsaturated acid, isomeric with pyrocinchonic acid, could be obtained either from the acid itself, or from the anhydride.

When ethyl dimethylethenylcarboxylate is treated with chlorine and the product hydrolysed, pyrocinchonic acid, dimethylethenylcarboxylic acid and the two isomeric dimethylsuccinic acids are obtained.

F. S. K.

Diacetyldicarboxylic Acid (Kepitic Acid) and Diacetyl. By R. Fittig, C. Daimler, and H. Keller (*Annalen*, 249, 182—214).

—Methods of preparing kepitic acid have been described by the authors (Abstr., 1887, 362) and by Wislicenus (*ibid.*, 587).

When an excess of bromine is added to a well-cooled solution of ethyl kepitate in carbon bisulphide and the solution is kept in a cold place for 12 hours, *monethyl dibromokepitate*,

$$COOEt{\cdot}CHBr{\cdot}CO{\cdot}CO{\cdot}CHBr{\cdot}COOH,$$

is deposited in transparent, colourless plates. The compound dissolves freely in chloroform and in water. It decomposes on exposure to the light or to a temperature of 70°. When bromine acts on a warm solution of ethyl kepitate in carbon bisulphide, *ethyl tetrabromokepitate* is formed; this substance crystallises in transparent prisms, soluble in carbon bisulphide. It melts at 119° and is not attacked by a solution of sodium carbonate at the ordinary temperature. Alcoholic ammonia decomposes the compound and yields oxamide and dibromacetamide. The ethyl salt of tetrachlorokepitic acid is formed when chlorine is passed into a boiling solution of ethyl kepitate in chloroform. Hantzsch and Zeckendorf (Abstr., 1887, 727) obtained this compound by acting on ethyl dihydroxyquinonedicarboxylate with chlorine. Ethyl kepitate forms, with 2 mols. phenylhydrazine, a crystalline compound, $C_2(N_2HPh)_2(CH_2{\cdot}COOEt)_2$, soluble in warm chloroform; it crystallises in pale yellow needles and melts between 160° and 180° with decomposition. Kepitic acid yields diacetyl or dimethyl diketone, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$, on dry distillation or on boiling with dilute sulphuric acid. Diacetyl is more conveniently prepared by the methods described by v. Pechmann (Abstr., 1888, 248 and 810). Hydroxylamine acts on diacetyl, forming the dioxime $OH{\cdot}N{:}CMe{\cdot}CMe{:}N{\cdot}OH$, a compound previously described by Schramm (Abstr., 1883, 573) under the name of ethylmethylacetoximic acid. The silver and copper salts of trimethylglyoxaline, $C_6H_9N_2Ag$ and $C_6H_9N_2Cu$, are precipitated when diacetyl is added to silver nitrate or cuprous chloride mixed with a large excess of ammonia. In the presence of a small quantity of ammonia, diacetyl deposits a mirror of metallic silver from a solution of the nitrate.

Dibromodiacetyl, $C_4H_4Br_2O_2$, prepared by adding bromine to a solution of diacetyl in carbon bisulphide, crystallises in flexible plates, melts at 116—117°, and is freely soluble in carbon bisulphide and chloroform. Diacetyl unites with hydrocyanic acid, forming the dicyanhydrin $CN{\cdot}CMe(OH){\cdot}CMe(OH){\cdot}CN$, a hygroscopic substance freely soluble in water, alcohol, and ether. It is decomposed by water at 100° into diacetyl and hydrocyanic acid, and is converted by strong hydrochloric acid at the ordinary temperature into dimethylracemic acid.

Dimethylracemic acid, $COOH{\cdot}CMe(OH){\cdot}CMe(OH){\cdot}COOH$, forms colourless crystals containing 1 mol. H_2O, and bears a close resemblance to racemic acid and also to Böttinger's dimethyltartaric acid. It is very soluble in water. The anhydrous acid melts with decomposition at 178—179°. The following salts were prepared: $C_6H_8O_6K_2$, needle-shaped crystals, freely soluble; $C_6H_9O_6K$, sparingly soluble in cold water. The calcium and barium salts (containing $1\frac{1}{2}$ and 2 mols. H_2O respectively) are obtained as crystalline precipitates on the

addition of calcium or barium chloride to a solution of the normal potassium salt.
W. C. W.

Some Nitramines and their Preparation. By A. P. N. FRANCHIMONT and E. A. KLOBBIE (*Rec. Trav. Chim.*, 7, 343—357).—*Methylurethane*, $NH_2·COOMe$, is obtained by dissolving the methyl salt of the nitro-derivative of ethylenediamidoformic acid (this vol., p. 124) in a strong aqueous or alcoholic solution of ammonia. It crystallises from ether in large plates melting at 55—56°, and boils under a pressure of 760 mm. at 176·5—177·5°. Ethylenedinitramine is simultaneously formed, as also a compound of the nitramine with ammonia, which is insoluble in ether but very soluble in water, and melts with decomposition at about 155—157°. The action of ammonia on the above methyl salt takes place in accordance with the equation $C_2H_4[N·(NO_2)COOMe]_2 + 2NH_3 = C_2H_4(NH·NO_2)_2 + 2NH_2·COOMe$.

By the action of methyl iodide (2 mols.) on ethylenedinitramine (1 mol.), a dimethyl-derivative, $C_2H_4(NMe·NO_2)_2$, is obtained, melting at 137°. A monomethyl-derivative, melting at 121—122°, is formed at the same time. Both these substances can be crystallised from water or absolute alcohol, the latter of the two being the more soluble.

By the action of methyl carbonate (2 mols.) on trimethylenediamine (1 mol.), a white substance is obtained, crystallising from ether, in which it is but slightly soluble, in oblique rhombic plates melting at 74—75°. Analysis shows that it is *methyl trimethylenediamidoformate*, $C_3H_6·(NH·COOMe)_2$. When treated with concentrated nitric acid, it is converted into *methyl trimethylenedinitramidoformate*,

$$C_3H_6[N(NO_2)·COOMe]_2,$$

which crystallises from alcohol in long needles or prisms melting at 89—90°. An aqueous solution of ammonia converts this last compound into a crystalline substance melting at 147°, which, when boiled with alcohol, loses ammonia and yields *trimethylenedinitramine*, $C_3H_6(NH·NO_2)_2$. The melting point of this compound is 67°. It is very soluble in water and alcohol, less so in ether and chloroform. It crystallises in short, thick prisms. When boiled with water containing 2 per cent. of sulphuric acid, it loses nitrous oxide. It has an acid reaction and gives metallic derivatives.

By treating pentamethylenediamine in a similar manner, an analogous series of compounds were obtained. *Methyl pentamethylenediamidoformate* crystallises from water or alcohol in slender needles melting at 114°. *Methyl pentamethylenedinitramidoformate* crystallises from ether and alcohol in small prisms melting at 37°. *Pentamethylenedinitramine* crystallises in oblong plates melting at 59—60°. It is very soluble in water and alcohol, and when boiled with water containing sulphuric acid loses nitrous oxide, giving at the same time an oily substance which is volatile in steam.

By treating monomethylamine with an aqueous solution of methyl chloroformate, methyl methylamidoformate, $NH·Me·COOMe$, is obtained, which, on nitrating, subsequent treatment with ammonia and boiling in alcoholic solution, gives *methylnitramine*, $NHMe·NO_2$. This nitramine crystallises in long, colourless, flat needles melting at 38°. It has a very acid reaction. By the action of methyl iodide and alcoholic potash, it is converted into dimethylnitramine.

Ethylnitramine, $NHEt\cdot NO_2$, may be similarly obtained from ethylamine. By evaporation of the alcoholic solution and cooling, crystals are obtained which melt at 3°.

The authors believe the method used for the preparation of the above nitramines from primary amines to be one of general application. H. C.

Paradiethylbenzene. By A. VOSWINKEL (*Ber.*, **22**, 315—317).—Paradiethylbenzene boils at 182—183°, and when boiled with dilute nitric acid yields parethylbenzoic acid and terephthalic acid.

Cadmium paradiethylbenzenesulphonate, $(C_6H_3Et_2\cdot SO_3)_2Cd + H_2O$, crystallises very readily in flat, colourless prisms, whereas the salt of the corresponding meta-acid is very readily soluble in water. The *sulphonamide*, $C_6H_3Et_2\cdot SO_2NH_2$, crystallises in microscopic needles and melts at 85°.

Tetrabromoparadiethylbenzene, $C_6Br_4Et_2$, crystallises in needles melting at 112°. The *nitro*-compound, $C_6H_3Et_2\cdot NO_2$, is a heavy, brownish liquid boiling at 155° (23 mm.) with partial decomposition. The *amido*-derivative is a bright-yellow liquid boiling at 140—142° (20 mm.); the *hydrochloride*, $C_{10}H_{15}N,HCl$, crystallises in colourless needles and turns reddish-brown on exposure to the air. *Acetoparadiethylanilide*, $C_6H_3Et_2\cdot NHAc$, crystallises in colourless plates and melts at 99°.

Paradiethylphenol, $C_6H_3Et_2\cdot OH$, prepared by melting the sulphonic acid with potash, is a yellowish liquid boiling at 126—127° (17 mm.). It is sparingly soluble in cold water, the solution having a burning taste and a phenol-like odour. Ferric chloride gives no coloration, but bromine-water produces a white precipitate in an aqueous solution.

Paradiethylthiophenol, $C_6H_3Et_2\cdot SH$, prepared by treating the sulphonic chloride with zinc-dust and reducing the salt obtained, is an almost colourless, disagreeably smelling liquid boiling at 113° (18 mm.) F. S. K.

Nitrobromocymene and Nitrochlorocymene. By M. FILETI and F. CROSA (*Gazzetta*, **18**, 290—297).*—*Mononitrobromocymene* from thymol, $C_6H_2PrMeBr\cdot NO_2$ [1 : 4 : 2 : 5], is obtained pure by adding the bromocymene (parapropylmetabromotoluene) (1 part) rapidly to nitric acid of sp. gr. 1·48 (5 parts), cooled to 12—15°, keeping the temperature within these limits whilst the mixture is occasionally agitated; after an hour, the product is poured into water, the oil well washed, and distilled in a current of steam. If no more than 30 grams are operated on at a time, it does not contain either a dinitro-compound or unaltered bromocymene. The pure mononitro-derivative is an oil which is heavier than water; it is rapidly oxidised by boiling with

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[*] The authors distinguish the bromine and chlorine derivatives obtained by the action of phosphorus perchloride or perbromide on *thymol* as chloro- or bromocymene from thymol, whilst those obtained from *cymene* by the action of bromine or chlorine are designated as chloro- or bromo-cymene from cymene.

nitric acid of sp. gr. 1·39, yielding bromonitrotoluic and melting at 199—200°. It dissolves in nitric acid of sp. gr. 1·52, cooled to 0°, with formation of two dinitro-derivatives.

Dinitrobromocymene (from thymol), $C_6H_2PrMeBr(NO_2)_2[1:4:2:5:?]$, is best prepared by allowing the bromocymene to drop slowly into nitric acid of sp. gr. 1·52 (5 parts), cooled to 0°. The product is then poured into water, the precipitate washed, pressed between filter-paper, and crystallised from alcohol. The crystals are a mixture of two isomeric dinitro-derivatives, which appear to be isomorphous, as they cannot be separated by crystallisation. Attempts to separate them by distillation with steam were equally fruitless. On agitating the finely powdered mixture with ether at the ordinary temperature, evaporating the solution and crystallising the residue repeatedly from alcohol, a compound was obtained with a constant melting point of 125—126°. The other isomeride, which seems to melt at about 94°, is also formed in small quantity along with bromonitrotoluic acid, when the mononitrobromocymene is treated with nitric acid of sp. gr. 1·39, as stated above. It could not be obtained in a pure state, however.

Mononitrochlorocymene (from thymol), $C_6H_2PrMeCl{\cdot}NO_2\,[1:4:2:5]$. This is prepared like the brominated derivative. Like the latter, it yields chloronitrotoluic acid melting at 180—181° when boiled with nitric acid of sp. gr. 1·39.

Dinitrochlorocymene (from thymol). Like the brominated derivative, the chlorocymene yields a mixture of two dinitro-derivatives, which could not be separated; one appears to melt at about 80°, the other was prepared in a pure state by Ladenburg and Engelbrecht by the action of phosphorus pentachloride on dinitrothymol.

Mononitrobromocymene (from cymene), $C_6H_2PrMeBr{\cdot}NO_2\,[1:4:3:?]$, is best prepared by allowing the bromocymene (parapropylorthobromotoluene) to drop slowly into cooled nitric acid, sp. gr. 1·48 (5 parts); the two liquids should be left in contact with occasional agitation for 8 to 10 hours and then poured into water. The product is washed with sodium carbonate solution to remove a little bromotoluic acid formed at the same time, distilled in a current of steam, dried over sulphuric acid in a vacuum, and distilled under diminished pressure (b. p. 210—211° at 100 mm.). It is a red liquid which distils at the ordinary temperature at 289—291° with partial decomposition.

Dinitrobromocymene (from cymene), prepared as already described. The product is a dark-red liquid which, after a time, deposits crystals; these, when separated, pressed, and recrystallised, form bright-yellow prisms which melt at 95—96°. The red oil is an isomeric dinitro-compound containing some of the solid in solution.

Mononitrochlorocymene (from cymene), prepared like the brominated derivative, is a dark-red liquid. The *dinitrochlorocymene* crystallises in bright-yellow prisms which melt at 109—110°. A liquid isomeride seems to be formed at the same time.

There is a marked difference in the action of light on these dinitro-derivatives, those from cymene rapidly becoming red on exposure, whilst the corresponding compounds from thymol are unaffected.

C. E. G.

Oxidation of the Chlorocymene and Bromocymene from Thymol and from Cymene. By M. FILETI and F. CROSA (*Gazzetta*, **18**, 298—313).—In a former paper (Abstr., 1887, 37) the authors showed that the chlorocymene from thymol when oxidised by nitric acid of sp. gr. 1·24 to 1·29, gave metachlorocumic, orthochloroparatoluic, and chloroterephthalic acids, whilst the brominated derivative, with acid of sp. gr. 1·20, gave bromocumic acid, and with acid of sp. gr. 1·29 the same product, together with bromonitrotoluic acid, bromoterephthalic acid, and bromonitrocymene. Acid of sp. gr. 1·39 gave the two acids last mentioned with mere traces of bromocumic acid.

The authors have repeated Landolph's and Gerichten's experiments on the oxidation of the bromo- and chloro-cymenes from cymene (*Ber.*, **5**, 268; **10**, 1249; and **11**, 366), and confirm their results, except that they found that the chlorocymene boils at 216—218° instead of at 208—211°, as stated by Gerichten.

The *bromonitrotoluic acid*, $C_6H_2MeBr(NO_2)\cdot COOH$ [1 : 3 : 6 : 4], is more conveniently prepared by oxidising mononitrobromocymene with nitric acid of sp. gr. 1·39 (preceding Abstract), as in this case no other acid is formed at the same time. The *calcium* salt, with $5H_2O$, crystallises in lustrous, yellowish prisms; and the *magnesium* salt, with $8H_2O$, in large, yellow plates. When reduced with sodium amalgam, it yields *metamidotoluic* acid, which crystallises in long, colourless plates, belonging seemingly to the trimetric system. It melts at 164—165°, and is identical with the acid obtained by Ahrens (*Zeitschr. f. Chem.*, 1869, 104) from metanitroparatoluic acid.

Orthamidometanitroparatoluic acid, $C_6H_2Me(NO_2)(NH_2)\cdot COOH$ [1 : 2 : 4 : 5]. When the bromonitrotoluic acid is heated with alcoholic ammonia at 180° for a day in sealed tubes, it is converted into a mixture of the amido-acid with nitrometatoluidine. These two are separated by evaporating the alcohol, and treating the residue with aqueous ammonia, when the amido-acid dissolves, leaving the nitrometatoluidine. On acidifying the ammoniacal solution, the acid is thrown down as a voluminous, yellow precipitate, which can be purified by crystallisation from dilute alcohol, when it forms long, silky, yellow needles, which contain 1 mol. H_2O, and melt at 235—236°.

The *nitrometatoluidine*, $C_6H_3Me(NO_2)\cdot NH_2$ = [1 : 2 : 5], which may be more conveniently prepared by heating bromonitrotoluic acid with fuming hydrochloric acid at 180°, melts at 135—136°, and is identical with the compound obtained by Beilstein and Kuhlberg from acetometatoluidide. When reduced with tin and hydrochloric acid in the usual way, it yields paratoluylenediamine melting at 64°, and boiling at 273—274°.

Orthobromometamidoparatoluic acid, $C_6H_2Me(NH_2)Br\cdot COOH$ = [1 : 2 : 5 : 4]. When bromonitrotoluic acid is heated at 120° with alcoholic ammonium sulphide for a day in sealed tubes, it is converted into the amido-acid, but at the same time resinous substances are produced, from which it is very difficult to separate it. It is far better to use ferrous oxide as the reducing agent, by dissolving the acid (10 grams) in excess of ammonia, and adding the requisite amount (64 grams) of ferrous sulphate in aqueous solution. The acid is only sparingly soluble in alcohol or ether, and moderately so in alcohol. It crystallises in plates which melt at 186—187°.

Paradibromoparatoluic acid, $C_6H_2MeBr_2\cdot COOH$ [1 : 2 : 5 : 4]. Bromamidotoluic acid dissolved in alcohol is mixed with an alcoholic solution of nitrous anhydride and ether added, until a precipitate begins to form; in a few minutes, the diazoamido-derivative separates as a whitish crystalline powder, which after being repeatedly washed with ether is treated with a solution of hydrogen bromide saturated at 0°, and the mixture gently heated at first and finally boiled. The acid is purified by crystallisation from boiling benzene. It forms long, colourless needles, or short, yellowish prisms which melt at 200—201°.

The *ethyl salt* crystallises in colourless, slender needles, which melt at 49°. This acid is identical with the acid Schultz obtained by oxidising paradibromoparaxylene (*Ber.*, **18**, 1762). He gives the melting point as 195°, as is shown by its yielding paradibromoterephthalic acid by oxidation with potassium permanganate. The true melting point of the last-mentioned acid is 316—317°, and its ethyl salt melts at 124—125°.

Orthobromoparatoluic acid, $C_6H_3MeBr\cdot COOH$ = [1 : 3 : 4], obtained by decomposing the diazoamidobromotoluic acid by boiling it with alcohol, crystallises in slender, colourless needles melting at 140—141°. It is easily soluble in alcohol, ether, and benzene, but only sparingly in water. The acid obtained by Kelbe and Koschnitzky (Abstr., 1886, 884) by oxidising a bromocymene with nitric acid, and described by them as orthobromoparatoluic acid, is either bromonitrotoluic acid or impure metabromotoluic acid, according as the bromocymene employed was derived from thymol or from cymene.

Chlorocymene from thymol, when oxidised with nitric acid of sp. gr. 1·39, yields a mixture of the two isomeric dinitrochlorocymenes already described (preceding Abstract) with chloronitrotoluic and chloroterephthalic acids; these two acids may be easily separated by taking advantage of the insolubility of the chloroterephthalic acid in benzene.

Chloronitrotoluic acid, $C_6H_2Me(NO_2)Cl\cdot COOH$ = [1 : (?) 2 : 5 : 4], crystallises in yellowish, flattened needles which melt at 180—181°. It is insoluble in water, moderately soluble in boiling benzene, soluble in alcohol and ether. The *barium salt* crystallises with 3½ mols. H_2O in yellowish needles; the *magnesium salt*, with 8 mols. H_2O, forms large, yellowish tables.

Chloroterephthalic acid, $C_6H_3Cl(COOH)_2$, obtained by the oxidation of chlorocymene, cannot be purified by crystallisation; it is necessary to first convert it into the methyl salt, purify it, and recover the acid by hydrolysis. The *methyl salt* crystallises from aqueous alcohol in colourless needles which melt at 59—60°; the acid is a white powder consisting of microscopic needles which melt at 300°.

C. E. G.

Behaviour of Phenols and Hydroxy-acids towards the Alkali Hydrosulphides. By F. Fuchs (*Monatsh.*, **9**, 1143—1147). The hydrogen of the hydroxyl of hydroxy-acids and phenols containing neither halogens nor nitro-groups is not displaced by metal on

treatment with an alkaline hydrosulphide; which, however, readily turns out the hydrogen of a carboxyl-group (compare this vol., p. 463).
G. T. M.

Nitrometacresols. By W. STAEDEL (*Ber.*, 22, 215—216).—The nitrometacresol melting at 56°, obtained by nitrating metacresol (compare Abstr., 1883, 662), has the constitution [OH : Me : NO_2 = 1 : 3 : 6], and the nitro-compound (m. p. 129°) produced in the same reaction has the constitution [OH : Me : NO_2 = 1 : 3 : 4]. Salts and alkyl-derivatives of both of these substances have been prepared and will be fully described in a subsequent paper. The ethyl-derivatives yield one and the same dinitro-compound [OEt : Me : $(NO_2)_2$ = 1 : 3 : 4 : 6], from which dinitrotoluidine [NH_2 : Me : $(NO_2)_2$ = 1 : 3 : 4 : 6] was obtained. The nitrotoluidines [NH_2 : Me : NO_2 = 1 : 3 : 6] and [NH_2 : Me : NO_2 = 1 : 3 : 4] were also prepared, and the corresponding nitrotoluenes were obtained from the three nitramido-derivatives.

Paramidometacresol gives a chloroquinoneimide with calcium hypochlorite; the salts and acetyl-derivative were also prepared.
F. S. K.

Constitution of the Anilic Acids. By J. U. NEF (*Amer. Chem. J.*, 11, 17—26).—Hydroxylamine hydrochloride reacts with nitranilic acid, *hydroxyammonium nitranilate*, $C_6O_4(NO_2)_2(NH_4O)_2$, being formed. It is a yellow, crystalline solid, soluble in water. When heated to a high temperature, it explodes. With cold concentrated nitric acid, nitranilic acid is liberated. When boiled with hydroxylamine hydrochloride in excess, it is decomposed.

Sodium nitranilate reacts with bromine-water, bromopicrin, sodium bromide, hydrogen bromide, and oxalic acid being the products. This reaction takes place quantitatively, and must be carried out at 0°.

Methyl- and acetyl-derivatives of nitranilic acid could not be prepared, and the author believes that the anilic acids are derivatives of tetraketohexamethylene.
J. W. L.

Action of Methyl Iodide and Potash on Phloroglucinol. By O. MARGULIES (*Monatsh.*, 9, 1045—1054).—The author has treated phloroglucinol (1 mol.) with potash (6 mols.) and methyl iodide, conducting the experiment in the same way as that adopted by Herzig and Zeisel (Abstr., 1888, 822), and has isolated the following compounds:—

Pentamethylphloroglucinol, $C_6HMe_5O_3$ [Me_2 : Me_2 : Me = 2 : 4 : 6], contains neither hydroxyl- nor methoxyl-groups, thus differing in constitution from the chief product obtained by Herzig and Zeisel (*loc. cit.*) with ethyl iodide. After several recrystallisations from ether, it melts sharply at 80°. *Trimethylphloroglucinol*, $C_6H_3O_3Me_3$, and *bi-secondary tetramethylphloroglucinol*, $C_{10}H_{14}O_3$, are both soluble in potash, and each contains an hydroxyl-group. The former crystallises from methyl alcohol in plates melting at 184°; the latter in small needles melting at 114°.
G. T. M.

Aniline Chlorate and Perchlorate. By C. GIRARD and L. L'HOTE (*Compt. rend.*, 108, 183—185).—When pure aniline is poured into chloric acid, acicular crystals of aniline chlorate separate immediately, and can be dried on porcelain. At about 20°, the salt inflames and leaves a carbonaceous residue. It can also be obtained on a large scale from aniline hydrochloride by double decomposition, provided that the salt is carefully neutralised by agitating it with aniline. 100 grams of the hydrochloride are dissolved in 200 grams of water and mixed with a solution of 82 grams of sodium chlorate in 125 grams of water, and the white, crystalline product is drained on a funnel which is cooled to 0°. It is very soluble in water, and takes fire when brought in contact with fuming nitric acid, Nordhausen acid, or concentrated sulphuric acid, but not with ordinary nitric acid or with strong hydrochloric acid. With the two last mentioned, it yields coloured products.

Aniline perchlorate is obtained in brilliant lamellæ by the direct union of aniline and perchloric acid. It is also formed by adding a solution of 30 grams of sodium perchlorate in 50 grams of water to a solution of 30 grams of neutral aniline hydrochloride in 60 grams of water. It is very stable in the air at the ordinary temperature, but if heated in a tube, it deflagrates and deposits carbon. In contact with fuming nitric acid, it inflames, but ordinary nitric acid and strong sulphuric acid have no action in the cold. On heating, nitric acid forms coloured products, sulphuric acid expels the perchloric acid.

C. H. B.

Dehydrothiotoluidine. By P. JACOBSON (*Ber.*, 22, 330—335).—*Dehydrothiotoluidine*, $C_{14}H_{12}N_2S$, is obtained when primuline (3 grams) (compare Green, *J. Soc. Chem. Ind.*, 7, 179) is heated at 190—200° with phosphorus (1 gram) and hydriodic acid of sp. gr. 1·7 (12 grams). It can also be obtained by heating paratoluidine (100 grams) with sulphur (60 grams) at 180—190° for 18 hours, and then at 200—220° for six hours. The crude powdered product is extracted with hot hydrochloric acid, precipitated from the solution with water, and dissolved in hydrochloric acid; the filtered and diluted solution is neutralised with ammonia, and the precipitated base recrystallised from alcohol. It forms almost colourless needles, melts at 190—191°, and is moderately soluble in hot alcohol, benzene, and ether, but only sparingly in cold alcohol; all the solutions show a blue fluorescence. It dissolves in warm, concentrated hydrochloric acid with an orange coloration, but is precipitated in an impure condition on adding water.

This compound is identical with the "thiotoluidine" described in the German patent No. 35790 (Dahl & Co.), and a base of the same composition can be isolated from the insoluble portion of the melt obtained according to the directions given in the patent.

The phenol, $C_{14}H_{10}NS{\cdot}OH$, is obtained when dehydrothiotoluidine is diazotised and the product boiled with water. It crystallises from alcohol in colourless needles, melts at 255—256°, and is moderately soluble in hot alcohol, but almost insoluble in benzene and ether. The alcoholic solution is colourless, but alkaline solutions show a blue fluorescence. The *acetyl*-derivative, $C_{14}H_{10}NS{\cdot}OAc$, crystallises from alcohol in colourless needles, melts at 131—132°, and is readily soluble in glacial acetic acid and hot alcohol. (Compare also Green, Trans., 1889, p. 228 *et seq.*).

F. S. K.

Metamidoparacresyl Methyl Ether. By L. LIMPACH (*Ber.*, 22, 348—353).—Metamidoparacresyl methyl ether crystallises from hot water, melts at 51·5°, boils at 235°, and is readily soluble in alcohol, ether, and benzene. (Compare Hofmann and v. Miller, Abstr., 1881, 592.) The *hydrochloride*, $C_8H_{11}NO,HCl + H_2O$, crystallises in prisms, and loses its water at 80—90°. The *acetyl*-derivative, $C_{10}H_{13}NO_2$, crystallises in plates, and melts at 110°. The *formyl*-derivative, $C_9H_{11}NO_2$, crystallises from alcohol in prisms, and melts at 86°.

Chlorocresyl methyl ether, [Me : OMe : Cl = 1 : 4 : 3], prepared from the amido-compound by Sandmeyer's reaction, is a yellow oil, boils at 210° (uncorr.), and is insoluble in alcohol, ether, and benzene.

Hydroxycresyl methyl ether, [Me : OMe : OH = 1 : 4 : 3], is obtained by diazotising the amido-compound, boiling the product with potash, and distilling with steam. It is a yellow, aromatic-smelling oil, boils at about 185° with partial decomposition, and is readily soluble in alcohol, ether, and benzene, but only moderately so in water.

The *hydrazine*-derivative, [Me : OMe : N_2H_3 = 1 : 4 : 3], is obtained by diazotising the amido-compound and reducing the diazochloride first in the cold with a solution of hydrogen sodium sulphite and then with warm acetic acid and zinc-dust; the boiling filtered solution is mixed with fuming hydrochloric acid, and the salt which separates is decomposed with soda. It is a crystalline compound melting at 45°.

Homomethylsalicylonitrile, [Me : OMe : CN = 1 : 4 : 3], is prepared from the amido-compound by Sandmeyer's method; the product is distilled with steam and fractionated. It is a yellow oil, which boils at 270°, and is converted into homomethylsalicylic acid when heated with potash. This acid crystallises in needles, melts at 70°, and is soluble in water, benzene, and light petroleum. The *silver* salt, $C_9H_9O_3Ag$, is moderately soluble in water. Since the methyl ether of this acid yields homosalicylic acid when treated with hydriodic acid, the constitution of amidoparacresyl methyl ether is [Me : OMe : NH_2 = 1 : 4 : 3].

Amidoazoparacresyl methyl ether,

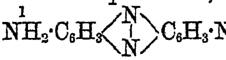
$$\overset{4}{OMe}\cdot C_6H_3\overset{1}{Me}\cdot\overset{3}{N}{:}N\cdot C_6H_2\overset{1}{Me}(\overset{4}{OMe})\cdot\overset{3}{NH_2},$$

is obtained when an alcoholic solution of amidocresyl methyl ether hydrochloride (5 grams), and the free base (10 grams) is treated with a solution of sodium nitrite (1·4 grams); hydrochloric acid is added, and the dark-red salt, which separates after a short time, is recrystallised from dilute hydrochloric acid and then decomposed with sodium carbonate solution. It crystallises from dilute alcohol in shining plates, melts at 156° with decomposition, and dissolves in acids with a red coloration.

F. S. K.

Oxidation of Orthophenylenediamine. By O. FISCHER and E. HEPP (*Ber.*, 22, 355—359).—When trianilidonaphthalene, [$(NHPh)_3$ = 1 : 2 : 4], is oxidised it is converted into rosinduline; a full account of the results will be published shortly.

It was observed by Griess (this Journal, 1872, 499) that orthophenylenediamine hydrochloride yields with ferric chloride a ruby-red, crystalline compound which he considered to be the hydrochloride of a base, $C_{12}H_{10}N_4$.. The authors prove that this base has the composition assigned to it by Griess, because, when the ruby-red salt is dissolved in water and the largely diluted solution poured into hot ammonia, diamidophenazine, $C_{12}H_{10}N_4$, separates on cooling in small, yellow needles. (Compare Salkowski, *Annalen*, **173**, 58.) No decomposition takes place as stated by Wiesinger (Abstr., 1884, 1322), and the results obtained by Rudolph (Abstr., 1880, 162) and Wiesinger (*loc. cit.*) are erroneous.

Diamidophenazine, the constitution of which is probably  $\overset{1}{NH_2}\cdot C_6H_3{<}\begin{matrix}N\\|\\N\end{matrix}{>}C_6H_3\cdot\overset{4}{NH_2}$, can be obtained in long, brownish-yellow needles by pouring a boiling, very dilute solution of the pure and sparingly soluble sulphate (prepared by dissolving the precipitated base in very dilute sulphuric acid and crystallising) into hot ammonia. It sublimes in slender, yellow plates when heated carefully in small quantities, and dissolves in concentrated sulphuric acid with a grass-green coloration which turns orange-red on diluting with water. It dissolves in benzene and alcohol with a greenish-yellow fluorescence; alcoholic solutions of the salts show a dark, orange-red fluorescence. The *diacetyl*-derivative, $C_{16}H_{14}N_4O_2$, separates immediately in yellow needles when the base is dissolved in acetic anhydride (10 parts) and the solution warmed. It turns brown when heated at about 200°, melts at about 270°, and is very sparingly soluble in all ordinary solvents, but can be crystallised from 20 per cent. alcohol.

Amidophenazine, $C_{12}H_9N_3$, sublimes in red needles when an intimate mixture of the diamido-compound (1 part) and zinc-dust (4 parts) is carefully heated. It crystallises from alcohol in long, red needles, melts at 265°, and is a strong base. It dissolves in concentrated sulphuric acid, forming an unstable, green salt which, on diluting with water, is converted into a stable, red salt. Dilute solutions of the base show an orange-red, solutions of the neutral salts a saffranine-red fluorescence. The *platinochloride*, $(C_{12}H_9N_3)_2,H_2PtCl_6$, crystallises from boiling water in feathery groups of brownish-red needles, and is very sparingly soluble in cold water.

When amidophenazine is treated with sodium nitrite and dilute sulphuric acid in alcoholic solution, it is converted into phenazine (azophenylene). Phenazine is also formed, together with amidophenazine, when the diamido-derivative (1 part) is distilled with zinc-dust (6—10 parts); it can be isolated by distilling with steam, as amidophenazine does not volatilise. F. S. K.

Benzyl-derivatives of Hydroxylamine. By R. BEHREND and K. LEUCHS (*Ber.*, **22**, 384—386).—When dibenzylhydroxylamine (m. p. 123°), prepared by treating hydroxylamine with benzylchloride according to Schramm's method (Abstr., 1884, 51), is heated at 130° with excess of benzyl chloride, the hydrochlorides of tribenzylamine and dibenzylamine are formed together with benzaldehyde and a basic oil, possibly tribenzylhydroxylamine.

Dibenzylbenzoylhydroxylamine, $BzN(C_7H_7)_2O$, is obtained when the dibenzyl-derivative is treated with benzoic chloride. It crystallises from alcohol in needles, melts at 97°, and is decomposed into dibenzylhydroxylamine and benzoic acid when boiled with alcoholic potash. *Benzoxycarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}OC_7H_7$, crystallises from alcohol in needles and melts at 139°.

When benzylhydroxylamine is treated with benzyl chloride (1 mol.) in presence of sodium carbonate, it is partially converted into a compound having the composition of dibenzylhydroxylamine and a neutral oil which seems to consist principally of tribenzylhydroxylamine; the neutral compound reduces Fehling's solution on warming. The dibenzyl-derivative is also an oil, and differs from the isomeric compound referred to above in having more strongly marked basic properties, and in its behaviour towards reagents. The *hydrochloride*, $NH(C_7H_7)_2O,HCl$, is very sparingly soluble in water. F. S. K.

Some Derivatives of Orthazotoluene. By V. POSPÉCHOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 608—610).—In a former paper (Abstr., 1888, 825) the author showed that orthazotoluene melts at 55° and not at 137°. On adding powdered orthazotoluene to fuming nitric acid of sp. gr. 1·400, it dissolves, and after some time the mixture solidifies to a crystalline mass. On treating this with water and recrystallising the product from alcohol, reddish-brown needles consisting of *mononitrazotoluene* are obtained; this melts at 87° and is soluble in alcohol, ether, benzene, and chloroform. If the nitric acid is stronger (sp. gr. 1·45), dark, reddish-brown crystals are obtained which are not perfectly homogeneous; they melt at 248—253° with volatilisation, and consist chiefly of *dinitrazotoluene*. B. B.

Orthonitrophenylhydrazine. By A. BISCHLER (*Ber.*, **22**, 240—241).—Orthonitrophenylhydrazine (Michael, Abstr., 1886, 699) is readily obtained by diazotising orthonitraniline and treating the product with stannous chloride and hydrochloric acid. It forms yellow needles of a silky lustre; the salts crystallise well.

Orthamidophenylhydrazine, prepared by reducing the above compound with stannous chloride and hydrochloric acid, forms white plates which soon become brown when exposed to air. N. H. M.

Azimido-compounds. By T. ZINCKE and H. ARZBERGER (*Annalen*, **249**, 350—372; compare Abstracts, 1887, 730—731, and 1888, 159). —*Bromazimidobenzene* is prepared by acting on an alcoholic solution of bromonitracetanilide [1 : 3 : 4] with dilute acetic acid and iron powder. When the reduction is accomplished, hot water is added to the mixture, the iron is precipitated by the addition of sodium carbonate, and the mixture is filtered hot. The filtrate is at once acidified with hydrochloric acid and mixed with sodium nitrite, when acetylbromazimidobenzene is deposited as a yellowish-white precipitate. This compound is decomposed by boiling with strong hydrochloric acid, yielding crystals of bromazimidobenzene, $C_6H_3BrN_3H$. This melts at 158—159°, and is freely soluble in alcohol and in glacial acetic acid. It is also soluble in alkalis, but is reprecipitated from its alkaline solutions by carbonic anhydride. It dissolves in sodium ethoxide, forming the sodium-compound $C_6H_3BrN_3Na$. Bromazimidobenzene forms compounds with acids as well as with metals. The hydrochloride and platinochloride, $(C_6H_3BrN_3H)_2,H_2PtCl_6$, are crystalline.

The acetyl derivative, $C_6H_3BrN_3Ac$, crystallises in needles, soluble in ether, benzene, and chloroform, and melts at 117—118°. Bromazimidobenzene unites with methyl iodide, forming *dimethylbromobenzeneazammonium iodide*, $C_6H_3BrN_3Me_2I$. This compound is decomposed by distillation in a vacuum, yielding methyl iodide and *methylbromazimidobenzene*, $C_6H_3BrN_3Me$; this is a crystalline compound which is soluble in alcohol, melts at 80° and forms a crystalline platinochloride. *Dimethylbromobenzeneazammonium chloride*, prepared by the action of silver chloride on the iodide, crystallises in needles. It is freely soluble in alcohol and in water, and melts with decomposition at 204°. The platinochloride crystallises in yellow needles and melts at 229°. The *chloriodine additive* product, $C_6H_3BrN_3Me_2Cl,ICl$, melts at 186—187°, and appears to crystallise in the monoclinic system.

Dimethylbromobenzeneazammonium bromide crystallises in needles soluble in alcohol and water; it melts at 206° with decomposition. The perbromide, $C_6H_3BrN_3Me_2Br,Br_2$, melts at 167°. *Dimethylbromobenzeneazammonium iodide* melts with decomposition at 200°. The periodide melts at 142—143°. *Dimethylbromobenzeneazammonium hydroxide* is known only in aqueous solution. It has a strongly alkaline reaction, and precipitates iron and copper salts from their solutions.

Benzylbromazimidobenzene, $C_6H_3BrN_3{\cdot}C_7H_7$, and *dibenzylbromobenzeneazammonium chloride*, $C_6H_3BrN_3Cl(C_7H_7)_2$, are prepared by heating at 100° a mixture of methyl alcohol (3 parts), benzyl chloride (3 parts), and bromazimidobenzene (2 parts). The crude product is evaporated and the residue dissolved in ether. Repeated treatment with water removes the azammonium chloride from the ethereal solution. The residue which remains on evaporating the ether becomes crystalline when moistened with methyl alcohol. After treatment with ammonia, it is purified by recrystallisation from dilute hydrochloric acid and from alcohol. Benzylbromazimidobenzene crystallises in silky needles, melts at 108°, and is soluble in alcohol and benzene. The *platinochloride*, $(C_6H_3BrN_3{\cdot}C_7H_7)_2,PtCl_6$, is crystalline. Dibenzylbromobenzeneazammonium chloride also forms a crystalline platinochloride.

Methylbenzylbromobenzeneazammonium iodide, $C_6H_3BrN_3(C_7H_7)MeI$, crystallises in needles and melts at 153—154°. The *chloriodochloride* melts at 123° with decomposition, and the *periodide* melts at 99°.

Trichlorobromazimidobenzene, $C_6Cl_3BrN_3H$, prepared by boiling the crude acetyl-derivative of bromazimidobenzene with nitrohydrochloric acid, melts between 246° and 250°, and is freely soluble in alcohol, benzene, and in acetic acid. This compound unites with bases but not with acids.

Methyltrichlorobromazimidobenzene, $C_6Cl_3BrN_3Me$, melts at 196°, and is insoluble in alcohol and acetic acid.

Dimethyltrichlorobromobenzeneazammonium iodide, $C_6Cl_3BrN_3Me_2I$, melts at 185°, and forms needle-shaped crystals which are sparingly soluble in water and have an intensely bitter taste. W. C. W.

Theory of the Formation of Aniline-blue. By R. Hirsch (*Chem. Zeit.*, **12**, 1725—1726).—The author endeavoured to prepare aniline-blue by heating together rosaniline and paratoluidine, and confirms Nietzki's statement that no blue is formed unless some organic acid is present. It was thought that the acids might form anilides, and that these reacted with the rosaniline to yield the blue; however, experiments with acetanilide and rosaniline, both with and without aniline, did not support this view. In another experiment, leucaniline, aniline, and benzoic acid were heated at 180° for two hours in a current of carbonic anhydride, when, contrary to expectations, the leucaniline remained unchanged, with the exception of a small quantity which became accidentally oxidised. The author thinks that the carbinol-group in the rosaniline takes some part in the formation of the blue. D. A. L.

Aldehyde-blue. By L. Gattermann and G. Wichmann (*Ber.*, **22**, 227—236).—Aldehyde-blue can be prepared by dissolving pararosaniline (5 grams) in a mixture of concentrated hydrochloric acid (55 grams) and water (55 grams), and, after adding aldehyde (22 grams) to the solution, keeping the mixture for 24 hours at the ordinary temperature. The whole is then diluted to 1 litre, the dye precipitated with sodium chloride, dried on porous plates, dissolved in absolute alcohol, and the filtered solution evaporated at the ordinary temperature. The same compound can also be prepared from pararosaniline and paraldehyde as described above; the yield is larger by this method, 10 to 12 grams of the pure substance being obtained from 10 grams of pararosaniline. It is a dark-blue powder, which on rubbing, or when compressed, shows a bronze-coloured metallic lustre. It is very hygroscopic and very readily soluble in water and alcohol, but insoluble in ether, benzene, and light petroleum. This dye is the hydrochloride of some base, but when treated with concentrated hydrochloric acid, it combines with a further quantity of acid, forming a reddish-yellow salt. The free *base* separates in light-red flocks when alkali is added to an aqueous solution of its salts. The salt shows all the properties of a rosaniline dye, and yields a colourless, amorphous leuco-base when reduced with zinc-dust and hydrochloric acid. The leuco-base dissolves in hydrochloric acid, forming a colourless solution which soon becomes blue on exposure to the air, and is rapidly converted into the original colouring matter by oxidising agents.

Aldehyde-blue yields a colourless, amorphous base when heated at 220° with concentrated hydrochloric acid; when heated alone, water and hydrogen chloride are evolved, but on raising the temperature a strong smell of quinoline is perceptible, and a heavy oil condenses and solidifies on the cooler portions of the tube. This substance, after purifying by dissolving in dilute hydrochloric acid, boiling with animal charcoal and reprecipitating, was obtained in colourless flocks; its composition is $C_{10}H_9N$, and it is probably a polymeric quinoline, because when quinaldine hydrochloride is heated at about 220°, an amorphous substance, identical in properties with that obtained from aldehyde-blue, is formed. It is readily soluble in alcohol, and the hydrochloric acid solution gives precipitates with platinic chloride, mercuric chloride, and bromine-water.

The *picrate*, $(C_{10}H_9N)_3,2C_6H_3N_3O_7$, is precipitated on adding picric acid to an alcoholic solution. The free base melts without decomposing, but has no well-defined melting point; when heated more strongly it is decomposed, but in a partial vacuum it boils without decomposition. The relationship between this base and Claus' diquinoline is shown also by the fact that both substances dissolve in hydrochloric acid with a red coloration. As this compound is probably a triquinaldine, aldehyde-blue is probably the chloride of *triquinaldylcarbinol*, $CCl(C_{10}NH_8)_3,HCl + 3H_2O$. This formula agrees fairly well with the analyses, and is also in accordance with the fact that nitrous acid has no action on aldehyde-blue.

A blue colouring matter, probably $C_{10}NH_7Me{\cdot}CCl(C_{10}NH_8)_2,HCl + 3H_2O$, is obtained by treating rosaniline with paraldehyde under the conditions stated above: this compound resembles aldehyde-blue in all its properties, and when heated, yields a compound very similar to triquinaldine.

Many attempts were made under various conditions to convert aldehyde-blue into aldehyde-green, but all were unsuccessful: when an aqueous solution of the blue is treated at 100° with hydrogen sulphide and sulphurous anhydride, a blue precipitate only is produced. Two distinct blue compounds are formed by the action of aldehyde on rosaniline: the sodium chloride filtrate from the aldehyde-blue contains a blue dye in solution. This substance is precipitated on adding alkali to the solution; it dissolves in hydrochloric acid with a blue coloration, and gives aldehyde-green when treated with hydrogen sulphide and sulphurous anhydride, but does not yield a blue precipitate. A light-green, amorphous base is precipitated when alkali is added to an aqueous solution of aldehyde-green; when this base is heated, the odour of both quinoline bases and sulphur-compounds is perceptible.

Aldehyde-blue can be suitably employed for staining microscopic preparations which have been hardened by alcohol.

A blue dye, different from aldehyde-blue, is obtained when aldehyde or paraldehyde and pararosaniline react at about 50°. This compound contains a larger proportion of chlorine and a smaller proportion of carbon than aldehyde-blue. F. S. K.

Silico-organic Compound of a new Type. By J. E. Reynolds (*Proc. Roy. Soc.*, **45**, 39—40).—A well-defined crystalline substance, *silicotetraphenylamide*, $Si(NHPh)_4$, is obtained by the action of silicon tetrabromide on excess of aniline dissolved in benzene, aniline hydrobromide being also formed. If the aniline is not in excess, the liberated bromine forms a brominated compound with it. The crystalline substance is purified by evaporation of the benzene solution, and crystallisation of the residue from carbon bisulphide. It forms short prisms, which melt at 136—137°, and do not decompose at

210°. When distilled at 80 mm. pressure, aniline and a substance, seemingly the silicon analogue of carbodiphenylimide, are obtained. It is anticipated that compounds similar to the above will be obtained from the homologues of aniline. H. K. T.

Aromatic Boron and Silicon Compounds. By A. MICHAELIS (*Ber.*, **22**, 241—243).—A reply to Gattermann (this vol., p. 344). Phenyl boron chloride, $BPhCl_2$, reacts with chlorobenzene and sodium with formation of *boron triphenyl*, which crystallises well and burns with a green flame when ignited. (Compare Michaelis and Becker, *Ber.*, **13**, 59, and Abstr., 1882, 731; Michaelis, *Annalen*, **229**, 397.) N. H. M.

Preparation of Terephthalaldehyde. By M. HÖNIG (*Monatsh.*, **9**, 1150—1153).—Paraxylenyl bromide, $C_6H_4(CHBr_2)_2$ [= 1 : 4], is obtained by acting on dry paraxylene, contained in a retort provided with an inverted condenser, and heated first at 140°, and eventually at 170° and 200°, with six times its weight of bromine previously dried over sulphuric acid. On cooling, almost the whole product crystallises in a mass of needles, the small quantity of oil remaining is removed by pressure, the crystals are washed with cold chloroform, and finally recrystallised from warm chloroform; the solution, on cooling, deposits large prisms which melt at 169°.

On heating paraxylenyl bromide with three times its weight of sulphuric acid (sp. gr. 1·825) at 120—130°, and pouring the product into water, terephthalaldehyde crystallises out in needles, which are quite pure after one recrystallisation from water. It melts at 116°, boils at 245—248°, and its compound with phenylhydrazine crystallises from alcohol in golden scales which melt with decomposition at 250°. G. T. M.

Acetophenone-derivatives. By C. ENGLER and O. ZIELKE (*Ber.*, **22**, 203—207).—Ethyl paranitrobenzoylacetate is a solid substance melting at 54—55°.

Paranitracetophenone is best prepared by mixing ethyl nitrophenylpropiolate with concentrated sulphuric acid, and keeping the mixture at 35—40° for 10 to 12 hours; the solution is then poured into water, boiled until the evolution of carbonic anhydride ceases, and the product recrystallised from carbon bisulphide and dilute alcohol. The *hydrazone* is crystalline, and melts at 132°.

Bromoparanitracetophenone, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$, is obtained by gradually mixing equivalent quantities of bromine and nitracetophenone in glacial acetic acid, then boiling, and lastly precipitating the ketone by adding water. It crystallises from a mixture of benzene and light petroleum, in needles, melts at 98°, and is soluble in acetone, glacial acetic acid, carbon bisulphide, ether, and hot alcohol. The *hydrazone* crystallises in yellow needles.

Paranitrobenzoyl carbinol, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OH$, is prepared by boiling the bromide with sodium acetate, first in glacial acetic acid and then in dilute acetic acid solution; it is a crystalline compound, melts at 121°, is readily soluble in warm alkalis, and yields a reddish, crystalline *hydrazone*.

Dibromoparanitracetophenone, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHBr_2$, is formed when a glacial acetic acid solution of nitracetophenone is boiled with rather more than the calculated quantity of bromine. It crystallises from a mixture of benzene and light petroleum in large, quadratic plates, which melt at 67·4°, and probably contain benzene; it is readily soluble in carbon bisulphide, acetone, glacial acetic acid and ether, but only sparingly in cold alcohol, and is not decomposed when boiled with water. When boiled with sodium carbonate, it yields paranitrobenzoic acid, parazoxybenzoylformic acid, and bromoform, but when treated in the cold with the calculated quantity of very dilute potash it is partially converted into nitrobenzoic acid and paranitromandelic acid (compare this vol., p. 508).

Parazoxybenzoylformic acid, $N_2O(C_6H_4{\cdot}CO{\cdot}COOH)_2$, is formed when dibromonitracetophenone is boiled with alkalis, and can also be obtained by boiling ethyl paranitromandelate with a concentrated solution of sodium carbonate, and decomposing the resulting sodium salt with hydrochloric acid. It separates from ether in yellow, nodular crystals, melts at 190°, and explodes when heated more strongly. The *potassium* and *ammonium* salts are readily soluble, but the *sodium* salt is only sparingly soluble in water. The *methyl* salt, $C_{18}H_{14}N_2O_7$, crystallises in yellow needles, melts at 173—175°, and is moderately soluble in benzene and glacial acetic acid, but only sparingly in alcohol. The acid gives a cherry-red coloration with strong sulphuric acid and benzene containing thiophen, and on diluting with water greyish-blue flocks are precipitated. When warmed with strong sulphuric acid, a gas, probably carbon monoxide, is evolved.

F. S. K.

Derivatives of Phenylacetic Acid and Phenylglyoxylic Acid. By G. HAUSKNECHT (*Ber.*, **22**, 324—330).—*Phenylacetodiethylamide*, $CH_2Ph{\cdot}CONEt_2$, is prepared by treating phenylacetic chloride with diethylamine in very dilute ethereal solution. It crystallises in nacreous plates, melts at 86°, and boils at 295—297° (corr.). It is not changed when treated with sodium ethoxide and benzyl chloride or with sodium ethoxide and isobutyl bromide.

Phenylacetodiphenylamide, $CH_2Ph{\cdot}CONPh_2$, prepared in like manner from phenylacetic chloride and diphenylamine, crystallises in small, yellowish needles melting at 72°. The hydrogen-atom in the methylene-group is not replaceable by alkyl radicles. The hydrogen in the methylene-group in the methyl salts of ortho- and para-nitrophenylacetate is not replaceable by alkyls.

Paranitrophenylacetic acid is oxidised to paranitrobenzoic acid when treated with nitrous acid in alkaline solution.

Methyl dinitrophenylacetateazotoluene, $C_{16}H_{14}O_6N_4$, prepared by treating methyl dinitrophenylacetate with diazotoluene (compare p. 516), crystallises in bright red needles, melts at 168°, and is sparingly soluble in cold alcohol.

Methyl dinitrophenylacetateazo-xylene, $C_{17}H_{16}O_6N_4$, crystallises in dark red needles melting at 159°.

Methyldinitrophenylacetateazonaphthalene, $C_{19}H_{14}O_6N_4$, crystallises in dark brown prisms, and melts at 94°. The last three compounds are all insoluble in aqueous alkalis.

Sodium methyldinitrophenylacetateazobenzenesulphonate,

$C_{15}H_{11}O_9N_4SNa$,

crystallises in small, yellow plates, and is readily soluble in water but insoluble in alcohol.

Diazobenzene chloride has no action on the two nitrophenylacetic acids.

The *silver* salts of ortho- and para-nitrobenzyl cyanide were obtained in an impure condition in the form of brownish-black precipitates, by treating the respective cyanides with potash and silver nitrate in alcoholic solution. *Lead orthobenzyl cyanide* is yellowish-brown, the *copper* salt is green. The *lead* salt of the para-compound is brown, the *copper* salt dark green.

Paranitrobenzoylphenylhydrazine, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}N_2H_2Ph$, is formed, with evolution of hydrogen cyanide, when paranitrobenzoic cyanide or chloride (1 mol.) is treated with phenylhydrazine (2 mols.). It crystallises in small, yellowish-red needles, melts at 198°, and is readily soluble in hot alcohol. It dissolves in alcoholic potash with a dark-violet coloration, which disappears on exposure to the air or on adding acid. It dissolves in warm, concentrated sulphuric acid with a blue coloration.

Paranitrobenzoyl cyanide gives a red coloration with an aqueous solution of sodium acetate, but no evolution of hydrogen cyanide takes place.

Benzoylphenylhydrazine (m. p. 169°) is formed when benzoic cyanide is treated with phenylhydrazine. F. S. K.

Nitrohydroxycinnamic Acids. By G. LUFF (*Ber.*, **22**, 291—299).—Metamidocinnamic acid (30 grams) dissolved in sulphuric acid (5 parts) and well cooled, was gradually treated with the calculated amount of potassium nitrate; the solution was then poured into water, and an excess of sodium nitrite added. The diazotised solution was afterwards boiled and filtered hot.

Orthonitrometahydroxycinnamic acid, $[COOH : OH : NO_2 = 1 : 3 : 6]$, separates from the solution obtained as just described in yellow flakes. It melts at 216°, and dissolves very readily in alcohol, very sparingly in hot water, ether, and acetic acid.

Orthonitrocoumaric acid, $C_9H_7NO_5$ $[COOH : NO_2 : OH = 1 : 2 : 3]$, is obtained from the filtrate from the above acid by boiling with basic zinc carbonate, decomposing the zinc salt with sulphuric acid, and extracting with ether. It melts at 218°, dissolves readily in hot water, ether, and dilute alcohol, sparingly in benzene, and hardly at all in chloroform. The *zinc salt* forms very slender, pale yellow needles, very readily soluble in alcohol. The acid has an intensely sweet taste.

Symmetrical metanitrohydroxycinnamic acid, $[COOH : OH : NO_2 = 1 : 3 : 5]$, is obtained by evaporating the mother-liquor from the above zinc salt, and treating the zinc salt which separates with dilute sulphuric acid. It forms lustrous crystals rather readily soluble in hot water, alcohol, and ether.

On repeating the above operations, the acid (m. p. 216°) was not again obtained; metahydroxybenzaldehyde was found in the product. The acid (m. p. 216°) is formed if the metamidocinnamic acid is first converted into the acetyl-compound.

Metahydroxycinnamic acid was prepared by suspending the amido-acid hydrochloride in water, diazotising with an excess of sodium nitrite, boiling the product, and filtering from resin. The yield was 75 per cent. of the theoretical.

Paranitrometahydroxycinnamic acid, [COOH : OH : NO_2 = 1 : 3 : 4], is obtained by slowly treating a solution of metahydroxycinnamic acid in glacial acetic acid with a slight excess of nitric acid (sp. gr. = 1·4); after some time reddish-brown crystals separate, and are crystallised from alcohol. It crystallises in gold-coloured needles melting at 248°, is extremely sparingly soluble in water, cold alcohol, and ether, practically insoluble in benzene and chloroform. Orthonitrocinnamic and metanitrometahydroxycinnamic acids are also formed.

The constitution of all four nitrohydroxycinnamic acids, as given, was determined by conversion into the corresponding nitrohydroxybenzoic acids. N. H. M.

Action of Methyl Iodide on Ethyl Phenylamidocrotonate. By M. Conrad and F. Eckhardt (*Ber.*, **22**, 83—86).—When ethyl phenylamidocrotonate (anilacetoacetate) is heated with methyl iodide at 130—140° for seven hours, it yields a product which on treatment with dilute ammonia divides itself into an oily and an aqueous layer. The oily layer contains ethyl acetate, aniline, and a compound, possibly dimethyltoluidine, boiling at 208°. The aqueous layer contains phenyllutidonecarboxylic acid; this acid, when heated at 270° until carbonic anhydride ceases to be evolved, is converted into phenyllutidone, which crystallises from water with 1 mol. H_2O (compare Abstr., 1887, 500). W. P. W.

Preparation of Nitromandelic Acids. By C. Engler and O. Zielke (*Ber.*, **22**, 207—209).—Orthonitromandelic acid (compare Engler and Wöhrle, Abstr., 1887, 948) can be prepared as follows:—Hydrochloric acid is gradually poured into a well-cooled mixture of dry potassium cyanide and an ethereal solution of orthonitrobenzaldehyde, the whole being constantly shaken; excess of methyl alcohol is then added, and hydrogen chloride passed into the solution. The hydrochloride of the imido-ether which separates is washed with ether, dissolved in water, and the solution filtered; after a short time, methyl orthonitromandelate separates from the solution. The free acid, obtained by hydrolysing the ethereal salt with sulphuric acid, is identical with the compound previously obtained from acetophenone. The yield is 15 to 20 per cent. of the theoretical quantity. The *methyl salt* melts at 74·5°, and is readily soluble in alcohol and ether, but only sparingly in light petroleum.

Paranitromandelic acid (compare p. 506) is easily obtained from paranitrobenzaldehyde as described above; the resulting methyl salt is hydrolysed with a mixture of equal volumes of water and concentrated sulphuric acid, and the free acid is extracted with ether. It crystallises from a mixture of ether and light petroleum, melts at 126°, and is readily soluble in acetone, glacial acetic acid, alcohol, and hot water, but only sparingly in chloroform, carbon bisulphide, and benzene. When treated with cold dilute alkalis, or when boiled with sodium carbonate, it is to a large extent converted into parazoxybenzoylformic acid, and when heated with concentrated sulphuric acid, carbon monoxide is evolved. The salts of the alkalis and alkaline earths are readily soluble. The *silver* salt is very sparingly soluble and is unstable. The *ethyl* salt, prepared by decomposing the imido-ether hydrochloride, crystallises from light petroleum in colourless needles melting at 75—76°. The *methyl* salt crystallises from benzene in prisms and melts at 87°. F. S. K.

Tautomeric Compounds. By J. U. Nef (*Amer. Chem. J.*, **11**, 1—17).—*Ethyl quinonediimidotetracarboxylate*, $C_6(NH)_2(COOEt)_4$, is prepared by adding bromine to a cooled solution of ethyl diamidopyromellitate.

It is a yellow solid, crystallising from alcohol in prisms which melt at 161°. It is volatile without decomposition, and dissolves readily in chloroform, benzene, and hot alcohol, with a pure yellow colour and without fluorescence. The alcoholic solution gives no coloration with ferric chloride; with zinc-dust and acetic acid, it is readily reduced to ethyl diamidopyromellitate.

With a view to determine whether the metal or alcohol radicle in the salts of ethyl quinoltetracarboxylate is united to carbon or to oxygen, the following compounds were prepared and studied:—

Ethyl sodioquinoltetracarboxylate, $C_6O_2Na_2(COOEt)_4$, prepared by the action of sodium ethoxide on ethyl quinoltetracarboxylate, separates as a red, gelatinous precipitate from the mixture. When dry, it is perfectly stable. With solutions of barium chloride, lead acetate, and cupric sulphate it forms yellow precipitates; silver nitrate is instantly reduced; with hydroxylamine hydrochloride, the original ethyl salt is regenerated. With methyl iodide, it forms a *dimethyl*-derivative, $C_6(MeO)_2(COOEt)_4$, melting at 95°; this crystallises in colourless needles, and is volatile without decomposition; its solutions fluoresce; with ferric chloride, it gives no coloration.

The corresponding *diacetyl*-derivative, $C_6(AcO)_2(COOEt)_4$, prepared by the action of acetic chloride on the dry sodium salt, is a colourless substance, volatile without decomposition, insoluble in alkalis, and melting at 120°. Its solutions show no fluorescence, and give no coloration with ferric chloride. It does not react with bromine.

In a similar series of experiments carried out with ethyl paradiketohexamethylenetetracarboxylate, the *sodium*-derivative was obtained by the action of sodium ethoxide on the diketo-compound. It is a pale-rose-coloured substance, and reacts with metallic salts and hydroxylamine in a manner exactly corresponding with the sodium-derivative of the quinol-compound. With bromine-water, it forms no additive compound, but is converted into the quinol-derivative. The *diacetyl*-derivative, $C_6(HO)_2Ac_2(COOEt)_4$, crystallises from alcohol in colourless needles melting at 142°. It gives a blood-red coloration with ferric chloride, dissolves in soda and sodium carbonate solutions, and its salts give reactions entirely analogous to those of the phenols.

With bromine-water, a product melting at 155° and containing no bromine is formed; it is not the diacetyl salt of the quinol-derivative. It forms an acetyl-derivative with acetic chloride, and reduces silver nitrate in the cold. J. W. L.

Derivatives of Resorcinoldisulphonic Acid. By F. ULZER (*Monatsh.*, 9, 1127—1131).—The author finds that the nitrogenous compound, which Fischer (Abstr., 1881, 1147) obtained in small quantity by the action of potassium nitrite on potassium resorcinoldisulphonate, is a salt of nitrosoresorcinoldisulphonic acid. It may be readily prepared in quantity by allowing a solution of potassium nitrite (20 grams) to drop slowly into a solution of potassium resorcinoldisulphonate (100 grams) in water (400 c.c.) and acetic acid (15 c.c.), the containing vessel being frequently shaken during the addition of the nitrite, after which it is allowed to remain in a warm place for several hours, and is cooled in ice-water, when violet-coloured crystals of *potassium nitrosoresorcindisulphonate*, $NO{\cdot}C_6H_4(OH)(SO_3K)_2{\cdot}OK$, are deposited.

On oxidation of potassium nitrosoresorcinoldisulphonate with 3 per cent. hydrogen peroxide or 2 per cent. permanganate, *potassium nitroresorcinoldisulphonate*, $C_6H(SO_3K)_2(OH)_2{\cdot}NO_2$, is obtained. It crystallises in golden-yellow prisms, its aqueous solution gives a deep blood-red coloured solution with ferric chloride, and on carefully warming with fuming nitric acid it furnishes styphnic acid. The corresponding *amidoresorcinoldisulphonic acid*, $C_6H(SO_3H)_2(OH)_2{\cdot}NH_2 + 3H_2O$, is obtained on reduction of the nitro-compound with tin and hydrochloric acid. It crystallises in silky needles which decompose at 240° without previously melting. G. T. M.

Preparation of Tetramethyldiamidotriphenylmethane. By M. NENCKI (*Monatsh.*, 9, 1148—1149; compare O. Fischer, Abstr., 1880, 40).—This base may readily be prepared in quantity by the following method:—A mixture of benzaldehyde (40 grams), dimethylaniline (100 grams), and 93 per cent. alcohol (40 grams) is placed in a large flask heated in a water-bath and provided with an inverted condenser. Phosphorus oxychloride (65 grams) is added very slowly from a dropping funnel, and the mixture is then heated for about half an hour, after which the product is dissolved in warm water, the solution filtered, and, when cold, treated with excess of soda. The oil thus obtained solidifies on standing, and on recrystallisation from alcohol furnishes pure tetramethyldiamidotriphenylmethane, the yield being nearly theoretical. G. T. M.

Diphenyl Ether and Dinitrodiphenyl Ether. By R. HIRSCH (*Ber.*, 22, 335—336).—Diphenol can be easily obtained by diazotising benzidine and boiling the product with water; 50 grams of benzidine yield 40—42 grams of diphenol.

Diphenyl ethyl ether, prepared by boiling diphenol (20 grams) with ethyl iodide (35 grams) and potash (12 grams) in alcoholic solution (150 grams), crystallises from glacial acetic acid in needles, melts at

174—176°, and is moderately soluble in hot alcohol, but insoluble in water.

Dinitrodiphenyl ethyl ether, obtained by nitrating the ether in glacial acetic acid solution, crystallises from alcohol, melts at 192—193°, and is converted into dinitrodiphenol when boiled with alcoholic potash.

Dianisidine can be prepared by boiling a glacial acetic acid solution of the dinitro-compound with tin and hydrochloric acid, and treating the product with nitrous acid. It yields colouring matters with naphthol- and naphthylamine-sulphonic acid. F. S. K.

Action of Nitrous Acid on Tetramethyldiamidobenzophenone and Analogous Compounds. By E. Bischoff (*Ber.*, **22**, 337—346; compare Abstr., 1888, 1197).—*Nitrosotetramethyldiamidobenzophenone picrate*, $C_{17}H_{19}N_3O_2,C_6H_3N_3O_7$, prepared by treating the ketone with picric acid in alcoholic solution, crystallises in orange-red needles melting at 150—152°. It is readily soluble in warm alcohol, but only sparingly in hot water, and insoluble in the cold. The *hydrochloride*, $C_{17}H_{19}N_3O_2,2HCl$, is precipitated when hydrogen chloride is passed into a benzene solution of the ketone; it is decomposed by water. The *mercurochloride* is a granular, crystalline compound. The *hydrazone*, $C_{23}H_{25}N_5O_3$, crystallises from hot alcohol in red needles, melts at 148°, and is soluble in hot alcohol, benzene, and hydrochloric acid, but insoluble in water.

Nitrosodimethamidobenzophenone, $COPh\cdot C_6H_2(NMe_2):NOH$, is obtained when sodium nitrite (2·15 grams) is gradually added to a dilute and well-cooled hydrochloric acid solution of dimethamidobenzophenone (7 grams); the oily product, which is precipitated on adding dilute sodium carbonate solution, is purified by dissolving in ether and shaking the solution with animal charcoal. It is a reddish-yellow oil, gives the nitroso-reaction, and yields an unstable hydrochloride. When reduced with tin and concentrated hydrochloric acid, it is converted into dimethamidobenzophenone.

Paradimethamidobenzoic acid (compare Michler, this Journal, 1876, ii, 68) is best prepared by heating an intimate mixture of tetramethyldiamidobenzophenone (1 part) and soda-lime (2—3 parts) at 340° for two hours, or distilling the mixture until no more dimethylaniline passes. The crude product is extracted with hot water, precipitated from the concentrated solution with dilute acetic acid, and recrystallised from alcohol. The *calcium* salt crystallises in yellowish plates.

Nitrosoparadimethamidobenzoic acid, $COOH\cdot C_6H_2(NMe_2):NOH$, is obtained when the preceding compound is treated with nitrous acid as described above. It crystallises from warm alcohol in yellow plates, melts at 224°, and is readily soluble in benzene, chloroform, and light petroleum, but only sparingly in ether. The *picrate*,

$$C_9H_{10}N_2O_3,C_6H_3N_3O_7,$$

crystallises in yellow needles melting at 168°. The *hydrochloride*, $C_9H_{10}N_2O_3,HCl$, crystallises in colourless needles, and is stable in the air. The *oxalate* melts at 178—181°. It also forms salts with platinic and mercuric chlorides. The nitroso-compound is reconverted into paradimethylamidobenzoic acid when heated with stannous chloride and concentrated hydrochloric acid.

Methyl paradimethamidobenzoate, $NMe_2{\cdot}C_6H_4{\cdot}COOMe$, crystallises from hot alcohol in plates, melts at 102°, and is readily soluble in benzene, ether, and chloroform, but only moderately so in dilute alcohol, and insoluble in alkalis.

Methyl nitrosoparadimethamidobenzoate, $OH{\cdot}N{:}C_6H_4(NMe_2){\cdot}COOMe$, crystallises from alcohol in golden-yellow plates, melts at 101°, and is readily soluble in ether and hot alcohol, but insoluble in water. It gives Liebermann's nitroso-reaction, is readily converted into the corresponding acid when boiled with alcoholic potash, and yields paradimethamidobenzoic acid when warmed with stannous chloride and concentrated hydrochloric acid. The *hydrochloride*, $C_{10}H_{12}N_2O_3,HCl$, crystallises in short, colourless needles. The *picrate*,

$$C_{10}H_{12}N_2O_3,C_6H_3N_3O_7,$$

crystallises in golden-yellow needles and is readily soluble in warm alcohol, but insoluble in water. The methyl salt also forms a platinochloride. F. S. K.

Derivatives of Deoxybenzoïn. By E. BISCHOFF (*Ber.*, **22**, 346—348).—*Propyldeoxybenzoïn*, prepared from sodiodeoxybenzoïn and propyl bromide, crystallises from alcohol in moss-like needles, melts at 33° and boils at 328—331° (corr.). The *oxime*, $CHPr^{\alpha}Ph{\cdot}CPh{:}NOH$, crystallises from alcohol in needles and melts at 100°. *Isopropyldeoxybenzoïn*, melts at 48° and boils at 324—326° (corr.). The *oxime* crystallises in needles and melts at 69—70°. The *hydrazone* crystallises in needles, melts at 72°, and decomposes on exposure to the air.

Hexyldeoxybenzoïn crystallises from alcohol in needles or plates, melts at 59°, and boils at 344—346° (corr.).

The *oxime*, $C_6H_{13}{\cdot}CHPh{\cdot}CPh{:}NOH$, crystallises in needles and melts at 89°.

Octyldeoxybenzoïn melts at 61° and boils at 350—355° (corr.). The *oxime*, $C_8H_{17}{\cdot}CHPh{\cdot}CPh{:}NOH$, crystallises in long needles and melts at 101°. F. S. K.

Benziles. By R. STIERLIN (*Ber.*, **22**, 376—383).—In preparing anisoïn by Bosler's method (Abstr., 1881, 421), it is best, as soon as the mixture has been boiled sufficiently, to cool directly and at the same time shake well for 15—20 minutes; the anisoïn then separates immediately in considerable quantities.

α-Anisildioxime, $OMe{\cdot}C_6H_4{\cdot}C(NOH){\cdot}C(NOH){\cdot}C_6H_4{\cdot}OMe$, is precipitated when anisil is boiled for a long time with excess of hydroxylamine hydrochloride in methyl alcohol solution. It is a crystalline powder, melts at 217°, and resembles α-benzildioxime in properties. It is soluble in hot glacial acetic acid and in dilute soda, but almost insoluble in alcohol, ether, and benzene. The *diacetyl*-derivative, $C_{20}H_{20}N_2O_6$, crystallises in prisms, melts at 139°, and is sparingly soluble in cold alcohol and glacial acetic acid.

β-Anisildioxime is obtained, together with the monoxime and other impurities, when the filtrate from the α-compound is evaporated. The pure compound is prepared by heating the α-derivative (1 part) at 160—170° with absolute alcohol (2—3 parts), or by heating a mixture of ainsil (2 parts) and hydroxylamine hydrochloride (1·2 parts) at 170° with absolute alcohol (6 parts) and two drops of concentrated hydrochloric acid. It crystallises in slender, colourless needles, melts at 195°, and is readily soluble in alcohol, glacial acetic acid, and soda. The *diacetyl*-derivative melts at 130° and is more readily soluble in alcohol and glacial acetic acid than the corresponding derivative of the α-oxime.

Anisiloxime, $OMe\cdot C_6H_4\cdot C(NOH)\cdot CO\cdot C_6H_4\cdot OMe$, is formed when an alcoholic solution of anisil (2 parts) is boiled for 10 minutes with hydroxylamine hydrochloride (1·2 parts). It separates from alcohol in crystalline aggregates, melts at 130°, and is readily soluble in ether, benzene, chloroform, and glacial acetic acid.

Paratoluoïn (*diparadimethylbenzoïn*,) $C_6H_4Me\cdot CO\cdot CH(OH)\cdot C_6H_4Me$, is obtained by boiling paramethylbenzaldehyde (10 parts) with potassium cyanide (2 parts) and 50 per cent. alcohol (30 parts) for about two hours, and then shaking the solution until the crystalline product separates. It crystallises in yellowish prisms, melts at 88—89°, and is readily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid, but only sparingly in hot water. It turns green when treated with fuming sulphuric acid. The *acetyl*-derivative, $C_{16}H_{15}O_2Ac$, melting at 100°, and the *benzoyl*-derivative, $C_{16}H_{15}O_2Bz$, melting at 119°, are colourless, crystalline compounds readily soluble in alcohol and ether.

Paratolil, $C_6H_4Me\cdot CO\cdot CO\cdot C_6H_4Me$, prepared by boiling toluoïn (1 part) with concentrated nitric acid (2 parts), crystallises from alcohol in yellowish plates, melts at 104—105°, and is soluble in ether, benzene, and glacial acetic acid. It gives a violet coloration when boiled with potash and absolute alcohol, and when treated with hydroxylamine hydrochloride, as described above, it yields two isomeric dioximes. The *α-dioxime*, $C_6H_4Me\cdot C(NOH)\cdot C(NOH)\cdot C_6H_4Me$, crystallises in plates or needles, melts at 217°, and is only sparingly soluble in alcohol, ether, and glacial acetic acid; the *acetyl*-derivative, $C_{20}H_{20}N_2O_4$, crystallises in prisms melting at 133—134°. The *β-dioxime* crystallises in needles, melts at 225°, and is readily soluble in alcohol; the *acetyl*-derivative melts at 144°.

Deoxytoluoïn, $C_6H_4Me\cdot CH_2\cdot CO\cdot C_6H_4Me$, prepared by reducing toluoïn with zinc and hydrochloric acid in boiling alcoholic solution, crystallises in needles, melts at 102°, and is readily soluble in ether and benzene, but insoluble in water; it is turned brownish-red by sodium ethoxide. The *benzyl*-derivative, $C_{23}H_{22}O$, crystallises in needles, melts at 92—93°, and is readily soluble in alcohol, ether, and benzene.

F. S. K.

Nitration of Naphthionic Acid. By R. NIETZKI and J. ZÜBELEN (*Ber.*, **22**, 451—453).—When sodium naphthionate is heated with acetic anhydride, it is readily converted into an acetyl-derivative which, on nitration in the cold, yields acetylamidonitronaphthalenesulphonic acid; the *ammonium* salt of this acid, $NO_2\cdot C_{10}H_5(NHAc)\cdot SO_3NH_4$, crystallises in yellow needles. *Nitronaphthylaminesulphonic acid*, $NO_2\cdot C_{10}H_5(NH_2)\cdot SO_3H$, is obtained by heating the acetylated derivative with dilute aqueous potash; it crystallises in colourless needles, yields red crystalline salts with alkalis, is readily diazotised, forming a diazo-compound yielding azo-dyes on treatment with amines or phenols, and is converted by the action of alkali into nitronaphthylamine (m. p. = 119°). It follows, therefore, that the constitution of the acid is $[NH_2 : SO_3H : NO_2 = 1 : 4 : 4']$. W. P. W.

Action of Phosphorus Pentachloride on β-Hydroxynaphthoic Acid. By H. RABE (*Ber.*, **22**, 392—396).—The *chloride*, $POCl_2\cdot O\cdot C_{10}H_6\cdot COCl$, is prepared by treating β-hydroxy-α-naphthoic acid with phosphorus pentachloride; it crystallises in white, satiny needles melting at 38°. When treated with water, or, preferably, allowed to remain exposed to the air for two days, it is converted into *α-carboxylnaphthyl-β-phosphoric acid*, $PO(OH)_2\cdot O\cdot C_{10}H_6\cdot COOH$, which crystallises in tufts of white needles, melts at 156°, and is readily soluble in water, alcohol, and acetone, sparingly soluble in benzene, and almost insoluble in light petroleum. The *silver* salt, $C_{11}H_6O_6PAg_3$, was prepared; the ammonium salt, on boiling its aqueous solution, decomposes into phosphoric acid, carbonic anhydride, and β-naphthol.

The chloride, when treated with absolute alcohol, yields a *diethyl* salt, $PO(OEt)_2\cdot O\cdot C_{10}H_6\cdot COOH$, which forms colourless, rhombohedral crystals, melts at 113°, is soluble in alcohol and ether, and decomposes when boiled with water. Phosphorus pentachloride reacts with the dichloride under pressure at 180—190°, forming *β-chloronaphthoic trichloride*, $C_{10}H_6Cl\cdot CCl_3$, a dark-brown, fluorescent oil which on exposure to the air is converted into *β-chloro-α-naphthoic acid*, $C_{10}H_6Cl\cdot COOH$. This is crystalline, melts at 152—153°, is readily soluble in alcohol and ether, and dissolves in 1000 parts of water at 20°, and in 126 parts at 100°. The *sodium* salt crystallises in thin, lustrous scales; the *calcium* salt, with 2 mols. H_2O, dissolves in 75 parts of hot and 150 parts of cold water; the *methyl* salt crystallises in white, broad, brittle prisms and melts at 50°. W. P. W.

Constitution of β-Naphthylamine-α-Sulphonic Acid. By C. IMMERHEISER (*Ber.*, **22**, 412—413).—The author points out that the formation of β-pyridinephenyleneketonesulphonic acid from β-naphthylamine-α-sulphonic acid (compare p. 527) is only possible if the compound is heteronucleal. Adopting the view ascribed to Cleve (*Ber.*, **20**, 75) and Forsling (*Ber.*, **20**, 2105) that β-naphthylamine-γ-sulphonic acid (Dahl's acid) has probably the constitution $[NH_2 : SO_3H = 2 : 4']$, the author points out that the alternative formula $[NH_2 : SO_3H = 2 : 1']$ must be that of β-naphthylamine-α-sulphonic acid. W. P. W.

Note by Abstractor.—Both Cleve and Forsling (*l. c.*) adopt provisionally the formula 2 : 1′ and not 2 : 4′ for the Dahl acid, and therefore the author's conclusions, based on the assumption made by Cleve and Forsling, would point to the formula 2 : 4′ and not 2 : 1′ as that of β-naphthylamine-α-sulphonic acid. Since the publication of this paper Armstrong and Wynne (Proc., 1889, 49, 50) have proved that the former acid has the constitution 2 : 4′ and the latter 2 : 1′.

W. P. W.

Constitution of β-Naphthol-α-Sulphonic Acid and β-Naphthol-α-Disulphonic Acid (R-Acid). By W. Pfitzinger and C. Duisberg (*Ber.*, **22**, 396—399).—When Bayer's β-naphthol-α-sulphonic acid is heated with ammonia in an autoclave, it is converted into so-called β-naphthylamine-α-sulphonic acid (Badische acid) which yields naphthalene-α-sulphonic acid when its amido-group is displaced by hydrogen by the hydrazine method. It follows, therefore, that each of these acids contains its sulphonic group in the α-position.

β-Naphthol-α-disulphonic acid (R-acid) when similarly treated yields Ebert and Merz's naphthalene-α-disulphonic acid, and consequently must contain a sulphonic group in a β-position in each nucleus.

W. P. W.

Note by Abstractor.—Since the publication of this paper, the constitution of the so-called β-naphthylamine-α-sulphonic acid (Badische acid) has been shown to be [$NH_2 : SO_3H = 2 : 1'$] (Armstrong and Wynne, Proc., 1889, 50); it follows, therefore, that β-naphthol-α-sulphonic acid has the constitution [$OH : SO_3H = 2 : 1'$]. In the same paper (p. 53) it is also shown that Ebert and Merz's naphthalene-α-disulphonic acid has the constitution 2 : 2′; consequently β-naphthol-α-disulphonic acid (R-acid) must have the constitution [$OH : SO_3H : SO_3H = 2 : 3 : 3'$].

W. P. W.

β-Naphthol-α-Sulphonic Acid. By R. Nietzki and J. Zübelen (*Ber.*, **22**, 453—456).—Naphthalene-α-sulphonic acid is obtained when β-naphthylamine-α-sulphonic acid, derived from β-naphthol-α-sulphonic acid, is diazotised and boiled with alcohol (compare preceding Abstract). When warmed with dilute nitric acid, β-naphthol-α-sulphonic acid is converted into a *dinitro*-derivative (croceïn-yellow) which forms a *dipotassium* salt, $OK\cdot C_{10}H_4(NO_2)\cdot SO_3K$, crystallising in golden-yellow scales, and a *potassium* salt,

$$OH\cdot C_{10}H_4(NO_2)_2\cdot SO_3K,$$

crystallising in long, yellow needles. On reduction with stannous chloride and hydrochloric acid, the dinitro-derivative is converted into the *hydrochloride* of *diamidonaphtholsulphonic acid*,

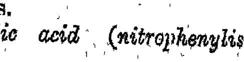
$$OH\cdot C_{10}H_4(NH_2)_2\cdot SO_3H,HCl,$$

which crystallises in colourless needles; it forms the *diimido*-derivative, $C_{10}H_8SN_2O_4$, on oxidation with ferric chloride, and yields a *diazo-compound*, $OH\cdot C_{10}H_4(NH_2)<\substack{SO_3\\ N_2}>$, crystallising in sparingly soluble green needles.

W. P. W.

Unorganised Ferments. By N. Kravkoff (*J. Russ. Chem. Soc.*, 1888, **20**, 623—632; comp. Abstr., 1888, 862).—In order to prepare diastase, barley-malt was ground and treated for half an hour with water at 35° to 40°; the liquid was then strained and filtered, and the solution saturated with powdered ammonium sulphate. The precipitate, after being collected, was washed with alcohol, treated with absolute alcohol for some time, dried at 35° to 40° and extracted with water. The solution thus obtained, when freed from salts by dialysis, was very limpid, gave none of the reactions of albuminoïds, and had a powerful action on starch. The following results in part confirm those obtained by Chittenden and Cummins (Abstr., 1885, 999), but in some respects are not in accordance with them. The mineral acids, hydrochloric, nitric, and sulphuric of 0·0002 per cent., and the organic acids, acetic and lactic, of 0·002 per cent., destroy the diastatic action of the ferment, and this action is not restored by 0·3 per cent. solution of sodium carbonate, or by albuminoïds; this action is found to depend on the strength of the acid, duration of action, and temperature. Carbonic acid in solution, but not gaseous carbonic anhydride, has a considerable retarding action. Alkalis show a retarding action merely; even a 5 per cent. solution of sodium carbonate does not stop the process. Neutral salts also act in the same way. In the stomach, however, owing to the presence of other compounds, especially albumins, globulins, and peptones, the action of diastatic substances is not stopped even in the presence of 0·2 per cent. hydrochloric acid (Schmidt), these substances having a protecting and sometimes even a stimulating action, as shown by direct experiment. For this purpose, the albuminoïd substance must be added first and then the acid, otherwise the fermentative process is stopped at once. This shows that starch may be actually converted into sugar in the stomach. It has been assumed hitherto, that ferments are incapable of diffusion through membranes; the author, however, shows that such a diffusion can take place, but that it depends on the medium below the dialysing membrane. Thus diastase diffuses very slowly into water, although its action on starch through a membrane is tolerably rapid; the action of pepsin and trypsin is much slower. The composition of diastase seems to be less complicated than that of trypsin and pepsin.

The author has found diastatic ferments in almost all animal tissues, and it seems that ferments may be regarded as products of decomposition of living protoplasm. B. B.

Ring-formation with Elimination of a Nitro-group from the Benzene Nucleus. By V. Meyer (*Ber.*, **22**, 319—323).—The compound $C_6H_3(NO_2)_2\cdot C(COOMe){:}N\cdot NHPh$, melting at 182—183°, is obtained when methyl dinitrophenylacetate is treated with a solution of diazobenzene chloride (compare A. and V. Meyer, Abstr., 1888, 693). If the yellowish-red alcoholic solution of this substance is mixed with a little potash (or soda), a deep blue solution of the salt $C_6H_3\cdot(NO_2)_2\cdot C(COOMe){:}N\cdot NKPh$ is formed; on keeping for a few minutes at the ordinary temperature, the blue solution turns bright-yellow and considerable quantities of a mixture of potassium nitrite and the benzopyrazole-derivative,  $NO_2\cdot C_6H_4{<}\begin{array}{l}C(COOK)\\NPh - N\end{array}{\gg}$, separates in the form of light-yellow crystals.

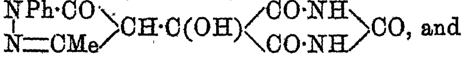
Nitrophenylbenzopyrazolecarboxylic acid (*nitrophenylisindazolecar-*

boxylic acid), $NO_2\cdot C_6H_4<\begin{matrix}C(COOH)\\NPh\text{—}N\end{matrix}\gg$, is obtained when the potassium salt is warmed for a long time with dilute sulphuric acid. It crystallises in small, pale-yellow needles, melts at 272°, turns brown at 265°, and is sparingly soluble in alcohol. The *methyl* salt is prepared by treating the acid with methyl alcohol and hydrogen chloride, first in the cold and then at a higher temperature; it crystallises in small, bright-yellow needles, melts at 191—192°, and gives a slight pyrazole-reaction. The compounds (hydrazones) which methyl dinitrophenylacetate yields with diazotoluene, diazo-xylene, and diazobenzenesulphonic acid, behave towards alkalis in the same way as that obtained from diazobenzene.

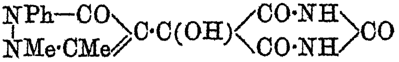
Methyl dinitrophenylacetate yields a deep-brown salt with alkalis, but no further change occurs under the conditions described above.

F. S. K.

Compounds of Alloxan with Pyrazolic Bases. By G. Pellizzari (*Gazzetta*, **18**, 340—344).—In a former memoir (Abstr., 1888, 142), the author showed that alloxan was capable of combining with amines with formation of new compounds; he has now investigated the compounds obtained by the action of phenylmethylpyrazolone and phenyldimethylpyrazolone (antipyrin). Aqueous solutions of alloxan dissolve these bases, and on heating the liquid to boiling for a few minutes, crystalline precipitates are obtained having the composition

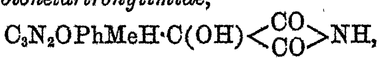


$$\begin{matrix}NPh\cdot CO\\ |\\ N{=}CMe\end{matrix}\!\!>CH\cdot C(OH)<\!\!\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\!\!>CO$$, and



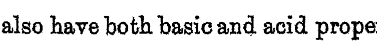
$$\begin{matrix}NPh\text{—}CO\\ |\\ NMe\cdot CMe\end{matrix}\!\!\gg C\cdot C(OH)<\!\!\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\!\!>CO$$

respectively. The latter, *phenyldimethypyrazolonetartronylcarbamide*, is but slightly soluble in water, and decomposes at 261°; the former, *phenylmethylpyrazolonetartronylcarbamide*, crystallises from water in long, yellow needles containing 3 mols. H_2O, and decomposes at 170—180°. They combine both with acids and with bases. When dissolved in cold aqueous potash, ammonia is produced, and on adding acetic acid to the solution much carbonic anhydride is evolved, and white crystalline precipitates are produced consisting respectively of *phenylmethylpyrazolonetartronylimide*,



$$C_3N_2OPhMeH\cdot C(OH)<\begin{matrix}CO\\CO\end{matrix}>NH,$$

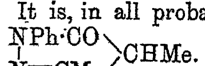
and *phenyldimethylpyrazolonetartronylimide*,



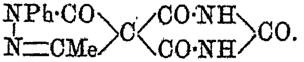
$$C_3N_2OPhMe_2\cdot C(OH)<\begin{matrix}CO\\CO\end{matrix}>NH.$$

These compounds also have both basic and acid properties. The former is easily decomposable; the latter crystallises from alcohol or water in colourless needles which melt with decomposition at 245—250°.

If instead of using cold aqueous potash, the substances just described are boiled with potash, a different reaction takes place. Under these circumstances, the antipyrin-derivative yields a substance of the composition $C_{12}H_{12}N_2O_2$; this is far more easily obtained, however, by boiling either of the antipyrin-derivatives with concentrated hydrochloric acid for some hours, and concentrating the solution. On cooling it deposits the hydrochloride, $C_{12}H_{12}N_2O_2,HCl + H_2O$, in white, lustrous needles. This hydrochloride loses acid on repeated crystallisation from water, the base, which is insoluble in water, being deposited. The base is insoluble in ether and benzene, but dissolves in hot alcohol, from which it crystallises on cooling in colourless, transparent prisms melting at 238° with decomposition. It is not acted on by acetic anhydride or by reducing agents, and it does not form compounds with phenylhydrazine or hydroxylamine.

When the phenylmethylpyrazolone-derivatives are boiled with potash, they are converted into "*phenylmethylmethoxypyrazolone*" (phenylmethylpyrazolone carbinol), $C_3N_2OPhMeH{\cdot}CH_2{\cdot}OH$, a substance crystallising in white nodules insoluble in water, ether, and benzene, but soluble in hot alcohol and in acetic acid. When heated at 180—185°, it loses a molecule of water, and is converted into *phenylmethylmethylenepyrazolone*, $C_3N_2OPhMe{:}CH_2$; this substance is more conveniently prepared, however, by merely boiling the alcoholic or acetic acid solution. It forms long, orange-yellow needles which melt at 178°. By the reducing action of zinc and acetic acid, it is converted into a compound which crystallises in slender, colourless needles melting at about 120°. It is, in all probability, a *phenyldimethylpyrazolone* of the formula  $\left.\begin{matrix}NPh{\cdot}CO\\ | \\ N{=}CMe\end{matrix}\right>CHMe$.

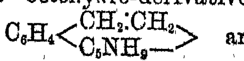
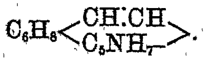
When treated with hydrochloric acid, the phenylmethylpyrazolone-derivatives undergo a totally different change. On boiling the tartronylcarbamide for a short time with concentrated hydrochloric acid, a new compound is precipitated in orange-red needles which decompose at 250° without melting. It is insoluble in water, and but little soluble in alcohol. As analysis showed that it was formed from the tartronylcarbamide by the elimination of H_2O, it in all probability is *phenylmethylpyrazolonemalonylcarbamide*,



$$\left.\begin{matrix}NPh{\cdot}CO\\ | \\ N{=}CMe\end{matrix}\right>C\left<\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\right>CO.$$

The oxidising action of nitric acid on these compounds completely destroys the alloxanic chain; in the case of the antipyrin-derivatives with formation of nitroantipyrin. C. E. G.

Reduction of Quinoline-derivatives. By E. BAMBERGER (*Ber.*, 22, 353—355).—Tetrahydroquinoline is not reduced by sodium and boiling amyl alcohol. When moist carbonic anhydride is passed into a solution of tetrahydroquinoline in light petroleum, a heavy, oily carbonate is precipitated, and gradually solidifies to a mass of colourless crystals.

β-Naphthaquinoline yields two isomeric octohydro-derivatives, which have probably the constitution  $C_6H_4\left<\begin{matrix}CH_2{:}CH_2\\ C_5NH_9{-}\end{matrix}\right>$ and  $C_6H_8\left<\begin{matrix}CH{:}CH\\ C_5NH_7{-}\end{matrix}\right>$. The former is produced in by far the larger quantity, and melts at 91°, the latter melting at 60°. Both compounds are easily obtained in crystals, and differ fundamentally both in chemical and physiological properties.

α-Naphthaquinoline, when treated in like manner, yields a crystalline octohydride, $C_6H_8<\genfrac{}{}{0pt}{}{CH:CH}{C_5NH_7}>$, which in its properties resembles the β-derivative melting at 60°. F. S. K.

Quinoline-derivatives from Ethyl Orthonitrobenzoylmalonate. By C. A. Bischoff (*Ber.*, **22**, 386—388).—*Ethyl α-ethoxy-γ-hydroxy-β-quinolinecarboxylate*, $OEt·C_9NH_4(OH)·COOEt$ [= 2′ : 4′ : 3′], is formed when ethyl orthonitrobenzoylmalonate dissolved in absolute alcohol is treated in the cold with zinc-foil and hydrogen chloride. It crystallises in small, colourless needles, melts at 107°, and the solutions give a violet coloration with ferric chloride.

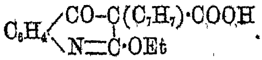
When ethyl orthonitrobenzoylmalonate is treated with hydrochloric acid and zinc-dust at the ordinary temperature, or if it is heated with zinc-dust and glacial acetic acid, various products are obtained, amongst which seem to be the ethereal salt described above, hydrogen ethyl salts, and *dihydroxyquinolinecarboxylic acid*, [$(OH)_2$: COOH = 2′ : 4′ : 3′]. This acid, which could only be isolated in the form of the silver salt, is converted into α-γ-dihydroxyquinoline (compare Baeyer and Bloem, Abstr., 1883, 197, and Friedländer and Weinberg, *Ber.*, **15**, 2683) when boiled for a long time with concentrated hydrochloric acid.

When ethyl orthonitrobenzoylmalonate is reduced with tin and hydrochloric acid in dilute alcoholic solution, α-γ-dihydroxyquinoline, α-ethoxy-γ-hydroxyquinoline, and various blue and green compounds are formed. The yield of the dihydroxy-derivative is 80 per cent.; none of the colouring matters are true dyes.

α-Ethoxy-γ-hydroxyquinoline crystallises in colourless needles and melts at 228°.

Azodihydroxyquinoline, $N_2[C_9NH_4(OH)_2]_2$ [N_2 : $(OH)_2$ = 3′ : 2′: 4′], is obtained when nitrosodihydroxyquinoline is treated with hydrogen sulphide in ammoniacal solution It is very stable, and dyes silk, wool. and unmordanted cotton-wool a bright orange-yellow.

Nitrodihydroxypyridinecarboxylic acid, [NO_2 : $(OH)_2$: COOH = 3 : 2 : 4 : 5 or 3 : 2 : 4 : 6], is formed when dihydroxyquinoline is treated with nitric acid. Ethyl benzylorthonitrobenzoylmalonate yields on reduction a hydrogen ethyl salt of a ketone acid. This compound melts at 147°, and has the constitution



$$C_6H_4<\genfrac{}{}{0pt}{}{CO-C(C_7H_7)·COOH}{N{=}C·OEt}$$

F. S. K.

Methylquinaldone and Methyllutidone. By M. Conrad and F. Eckhardt (*Ber.*, **22**, 73—83).—*γ-Hydroxyquinaldine methiodide*, $C_{10}H_9NO,MeI + H_2O$, is obtained by heating sodium hydroxyquinaldine with methyl iodide and benzene at 140° for about three hours. It crystallises in long, satiny needles, and when anhydrous, melts at 201°. When heated in aqueous solution with silver chloride, it is converted into the corresponding *chloride*, $C_{10}H_9NO,MeCl + H_2O$, which crystallises in well-formed, prismatic crystals, melts at 217°, and yields a crystalline *platinochloride*, $(C_{11}H_{12}NO)_2PtCl_6$, melting at 240° with decomposition.

γ-Methoxyquinaldine methiodide, $C_{11}H_{11}NO,MeI$, is prepared by heating γ-methoxyquinaldine with benzene and the calculated quantity of methyl iodide at 80—100° for some hours. It crystallises in white, lustrous needles, melts when anhydrous at 201°, is sparingly soluble in cold water, and yields methyl-γ-quinaldone (Abstr., 1887, 680) on treatment with silver oxide suspended in water.

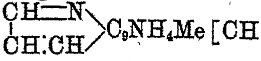
γ-Chloroquinaldine methiodide crystallises in greenish-yellow, needle-like forms.

Lutidone methiodide, C_7H_9NO,MeI, is formed by heating lutidone with methyl alcohol and an excess of methyl iodide at 140° for some hours. It is crystalline, melts when anhydrous at 242°, is readily soluble in water and methyl alcohol, and on decomposition with silver oxide is converted into methyllutidone (Abstr., 1887, 500).

Methoxylutidine is prepared by heating chlorolutidine at 150—160° with a solution of sodium methoxide in alcohol. It boils at 203°, and has a sp. gr. = 1·1011 at 24° compared with water at 15°. The *platinochloride*, $(C_8H_{12}NO)_2,H_2PtCl_6$, is a yellow, crystalline compound sparingly soluble in water; the *methiodide*, $C_9H_{14}NOI$, crystallises in long, white prisms, melts at about 204° with decomposition, and is converted into methyllutidone by treatment with silver oxide and water.

Ethoxylutidine is obtained by heating chlorolutidine with a solution of sodium ethoxide in alcohol. It is a colourless oil which boils at 215° without decomposition, and yields a crystalline *methiodide*, $C_{10}H_{16}NOI$; this melts at 196°, and on digestion with silver oxide is converted into methyllutidone. W. P. W.

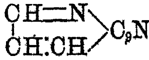
Metamidoquinaldine. By GERDEISSEN (*Ber.*, 22, 244—254).—Ortho- and meta-amidoquinaldine are prepared from the corresponding nitro-derivatives. Dry quinaldine nitrate (100 grams) is gradually added to sulphuric acid (1 kilo.), and after half an hour the mixture is diluted with water (3 litres), and nearly neutralised with solid sodium carbonate. The very small amount of resin which separates on neutralising is readily removed; and on treating the acid solution with a small amount of aqueous soda (so that it still remains acid) the orthonitro-compound separates; it is then collected, treated with an excess of soda, and kept in a cool place. The yield is 37 grams of ortho- and 56 grams of meta-nitroquinaldine. The reduction to amido-derivatives is best effected by adding the nitro-compound (30 grams) to an amount of stannous chloride sufficient to reduce 40 grams, and boiling.

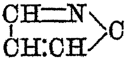
Methylphenanthroline, 
$\left.\begin{matrix}CH{=}N\\ |\\ CH{:}CH\end{matrix}\right\rangle C_9NH_4Me$ [CH : N : Me = 1 : 2 : 2′], is obtained together with an isomeride when a mixture of metamidoquinaldine (100 grams), glycerol (320 grams), and orthonitrophenol (75 grams), is gradually treated with sulphuric acid (270 grams). Amidophenol and hydroxyquinoline are also formed. The dark oily mixture of bases obtained is treated with hydrochloric acid, and the crystals covered with alcohol. The salt is then dissolved in water,

treated with ammonia, and extracted with benzene; the solution is dried with potash, distilled, and the crystalline residue extracted with ether, which dissolves only the methylphenanthroline. This is further purified by repeatedly crystallising the hydrochloride from alcohol. The free base, with 3 mols. H_2O, melts at 49—50°; it loses its water when kept over sulphuric acid, and then melts at 64—65°. It boils at above 360°, dissolves readily in cold benzene, and is soluble in boiling water, aqueous and absolute alcohol, and in ether, sparingly soluble in light petroleum. The *hydrochloride*, with 1 mol. H_2O, crystallises in needles, dissolves readily in hot water, and is soluble in hot aqueous alcohol, insoluble in ether; the *sulphate*, with 1 mol. H_2O, crystallises from alcohol in slender, silky needles; the *picrate* forms slender, sulphur-coloured needles melting at 216—217°; the *chromate* crystallises from water in very lustrous, red prisms; the *platinochloride*, with 1 mol. H_2O, the *ethiodide* (with 2 mols. H_2O), melting at 100—110°, and the *platinochloride* of the *ethochloride*,

$$C_{13}H_{10}N_2,EtCl,H_2PtCl_6,$$

are described. When methylphenanthroline is oxidised with permanganate, a *phenanthrolinecarboxylic acid*, $C_{12}H_7N_2{\cdot}COOH$, is obtained. This crystallises in pale yellow needles which melt at 208—209°, and decompose at 210° with evolution of carbonic anhydride and formation of Skraup's phenanthroline.

The *isomeric base*, $C_{13}H_{10}N_2 + 4H_2O$, crystallises from dilute alcohol in lustrous, concentrically grouped needles melting at 81—82°; the anhydrous base melts at 108—109°. It dissolves readily in hot benzene and hot dilute alcohol, and is insoluble in cold ether and cold light petroleum. It distils without decomposition. It has the constitution  $\left.\begin{matrix}CH{=}N\\ |\\ CH{:}CH\end{matrix}\right> C_9NH_4Me$ [N : CH : Me = 2 : 3 : 2′].

Methylphenanthroline,  $\left.\begin{matrix}CH{=}N\\ |\\ CH{:}CH\end{matrix}\right> C_9NH_4Me$ [N : CH : Me = 1 : 2 : 2′], prepared from orthamidoquinaldine, glycerol, orthonitrophenol, and sulphuric acid, crystallises with 2 mols. H_2O and melts at 53°; the anhydrous base melts at 75—76°. It dissolves very easily in hot benzene, readily in chloroform, rather readily in glacial acetic acid, and sparingly in ether and in light petroleum. It does not distil without decomposition. N. H. M.

Metaquinaldineacrylic Acid and Metaquinaldinealdehyde.

By F. ECKHARDT (*Ber.*, **22**, 271—285).—*Metaquinaldineacrylic acid*, $C_{13}H_{11}NO_2$, is prepared by the action of strong hydrochloric acid (300 grams) on metamidocinnamic acid hydrochloride (60 grams) and paraldehyde (45 grams) at 150°. The product is treated with water, freed from resin, and evaporated. The crystals of the crude hydrochloride (12 grams) are dissolved in water and treated with a solution of sodium acetate (12 grams), and quickly filtered from the resin which separates; after some time the free acid separates. This is repeatedly crystallised from hot alcohol and decolorised by means of animal charcoal. It forms small, slightly yellowish, monoclinic prisms, melts at 246° with decomposition, is very sparingly soluble in ether, chloroform, and light petroleum, more soluble in alcohol, benzene, and acetone. It has an acid reaction, and has at the same time basic properties, being readily soluble in dilute alkalis, less soluble in dilute acids. When heated, a small amount of a sublimate of slender needles melting at 223° is formed. The *hydrochloride*, $C_{13}H_{11}NO_2,HCl + H_2O$, crystallises in rhombic needles; it is easily dissociated; the *nitrate* (with 1 mol. H_2O) forms long, lustrous needles readily soluble in water; the *chromate* crystallises in orange-red needles; the *platinochloride* (with 2 mols. H_2O) crystallises in yellow needles; the *picrate* (with 1 mol. H_2O) separates from the alcoholic solution in groups of hair-like needles, soluble in alcohol, acetone, hot water, and acetic acid; the anhydrous salt melts at 150—152°. The *silver salt* (with 2 and 4 mols. H_2O) and the *calcium salt* (with $1\frac{1}{2}$ mol. H_2O), which crystallises in slender needles, are described. The neutral solution of the ammonium salt gives precipitates wiih various metallic salts which are described.

An *isomeric metaquinaldineacrylic acid* was obtained on one occasion from the alcoholic mother-liquor from the above acid. It crystallises in monoclinic plates (with 1 mol. H_2O) melting at 184°; it also crystallises with $\frac{1}{2}$ mol. EtOH and melts then at 204°. The *hydrochloride* crystallises in groups of very slender needles. The acid differs from that described above in the behaviour of its ammoniacal solution towards calcium and barium chlorides and magnesium sulphate: the one gives precipitates, the other does not.

Metaquinaldinealdehyde, $C_{11}H_9NO$, is obtained by dissolving the acid (10 grams) in sodium carbonate, diluting with water (500 c.c.), and adding benzene (250 grams); the whole is then cooled to 0° and gradually treated with a 6 per cent. solution of permanganate (10 grams). After 12 hours, it is filtered through calico, and the benzene separated and evaporated down; the oil thus obtained solidifies when cooled and is crystallised from light petroleum. It is purified by steam distillation. It forms white, matted hairs melting at 73°, which are readily soluble in benzene, ether, acetone, and alcohol, less so in light petroleum and hot water. The hot aqueous solution has a penetrating, unpleasant odour. The anhydrous salt melts at 61°. It reduces ammoniacal silver solutions, and yields a double compound with hydrogen sodium sulphite. The *hydrochloride* crystallises in pale-yellow needles; the *picrate* forms slender, matted needles, which blacken at 174°, and melt at 182° with decomposition; the *platinochloride*, $(C_{11}H_9NO)_2,H_2PtCl_6$, crystallises in orange-coloured, triclinic plates, melts at 211°, and is sparingly soluble in hot alcohol. When the aldehyde is heated with quinaldine and zinc chloride at 150°, a compound melting at 69° is formed. The *hydrochloride* of the phenylhydrazine-compound forms long, very thin, brick-coloured, matted hairs; the *sulphate*, $(C_{17}H_{15}N_3)_4,3H_2SO_4 + 9H_2O$, crystallises in small, brick-red needles. When metaquinaldinealdehyde (0·5 gram) is boiled with silver oxide (from 2 grams of silver nitrate), it is converted into Döbner and v. Miller's metaquinaldinecarboxylic acid (*Abstr.*, 1884, 1200).

Quinaldineacrylic acid (10 grams) was heated on a water-bath with pure chloral (35 grams), and the pulverulent hydrochloride thus formed extracted with alcohol. On evaporating the alcohol, a black, resinous substance was obtained, which was treated with hydrochloric acid; the light brown solution was precipitated with sodium carbonate, and the *trichloro-derivative*, $C_{12}NH_8O_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, which separated, crystallised from alcohol. It forms colourless prisms melting at 201°. The *hydrochloride*, $C_{15}NH_{12}Cl_3O_3,HCl$, was repeatedly crystallised from alcohol and decolorised with animal charcoal. It crystallises in slender prisms melting above 300°. The *silver salt*, $COOAg{\cdot}CH{:}CH{\cdot}C_9NH_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, crystallises in slender, white needles. When the resinous condensation product is treated with strong instead of with weak hydrochloric acid, the hydrochloride of a compound is obtained which only dissolves in hot caustic alkalis. This *hydrochloride* melts at 217°; the *free base*, which has the formula $C_{28}N_2H_{25}O_6Cl_5$, crystallises in needles melting at 128°.

α-Metaquinolinediacrylic acid, $C_9NH_5(CH{:}CH{\cdot}COOH)_2$, is obtained when the hydrochloride of the above trichlorinated derivative (9 grams) is heated on a water-bath with a solution of potassium carbonate (10 grams) in water (110 grains) for three hours, the product being filtered and fractionally precipitated with sodium carbonate. It melts at above 300°, is insoluble in water, sparingly soluble in hot alcohol.

N. H. M.

2′ : 3′-Dimethylquinoline. By G. Rohde (*Ber.*, **22**, 267—271). —2′ : 3′-Dimethylquinoline (Abstr., 1887, 974) crystallises in the rhombic system and boils at 261° (uncorr.) under 729 mm. pressure (not 255—260°). The platinochloride blackens at 230°; the picrate melts at 225°. The *chromate*, $(C_{11}H_{11}N)_2,H_2Cr_2O_7$, crystallises in orange-coloured spear-heads which become brown at 150° and decompose completely at 185°; the *hydrochloride*, $C_{11}H_{11}N,HCl + 2H_2O$, forms concentrically grouped needles of a vitreous lustre, very readily soluble in water and alcohol; the *sulphate*, $C_{11}H_{11}N,H_2SO_4 + H_2O$, crystallises in slender, concentrically grouped needles, extremely soluble in water, moderately soluble in alcohol, it melts at 235°; the *nitrate* crystallises in prisms very readily soluble in water and alcohol. The *methiodide*, $C_{11}H_{11}N,MeI + \frac{1}{2}H_2O$, crystallises from alcohol in groups of bright yellow, bent needles, melting at 218°. When 2′ : 3′-dimethylquinoline dissolved in sulphuric acid is treated with sufficient chromic acid to oxidise one methyl-group, an acid is obtained which is identical with Friedländer and Göhring's α-methylquinoline-β-carboxylic acid (Abstr., 1883, 1149).

The base obtained by the condensation of quinaldine with benzil (*loc. cit.*) has the formula $C_9NH_4Me{\cdot}CH{:}CPh{\cdot}COPh$; it melts at 176° (not 173°) and has a striking resemblance to acridine; the solutions of the salts show an intense green fluorescence. When heated for some hours at 180°, it is converted into a *polymeride*, which forms yellow crystals melting at 240°; this is a very feeble base and is extremely insoluble in the usual solvents. All attempts to effect a condensation between the methyl-group of the dimethylquinoline and the carbonyl-group of the benzil were unsuccessful.

N. H. M.

Action of Acetone on Ortho- and Para-amidophenol. By C. ENGLER and A. BAUER (*Ber.*, **22**, 209—215).—*Orthohydroxy-α-γ-dimethylquinoline*, $C_9NH_4Me_2{\cdot}OH$ [= 2′ : 4′ : 1], is formed together with methane when dry orthamidophenol hydrochloride (1 mol.) is heated with acetone (3 mols.) for 48 hours at 170—180°. The crude product is extracted with hydrochloric acid and acetone, and the mixed solutions distilled with steam to remove acetone and condensation products. The solution is then concentrated, partially neutralised with soda, filtered from resinous products, and the basic substances precipitated with sodium carbonate, excess being carefully avoided. The precipitate is washed with hot water, dried, dissolved in absolute alcohol, and concentrated sulphuric acid added to the solution; the precipitated crystalline sulphate, a further quantity of which can be obtained by adding ether to the alcoholic solution, is washed with alcohol and ether, dissolved in water, and, after evaporating the alcohol, potassium dichromate is added to the cold solution. The crystalline dichromate is decomposed with dilute sodium carbonate, and the base, which is precipitated in a flocculent condition, is crystallised from ether. Hydroxydimethylquinoline crystallises in prisms, melts at 65°, and boils at 281° (uncorr.). It is readily soluble in ether, benzene, alcohol, acetone, and chloroform, but only sparingly in light petroleum, and almost insoluble in water. It is slightly volatile with steam, sublimes when heated, and has an intensely bitter taste and the peculiar odour of quinoline-derivatives. It dissolves in soda, the solution giving orange or red precipitates with diazochlorides; the colouring matter obtained with β-naphthylamine dyes silk yellowish-brown. In a neutral solution of the base, ferric chloride gives a green coloration, which disappears slowly on heating but immediately on adding acids. A yellow, crystalline substance is precipitated when water is added to a hot alcoholic solution which has been previously mixed with bromine. The *sulphate*, $C_{11}H_{11}NO,H_2SO_4$, crystallises in slender needles and is soluble in water but only sparingly in hot absolute alcohol. The *hydrochloride* crystallises from hot concentrated hydrochloric acid or alcohol in yellowish, anhydrous plates, and is readily soluble in water but insoluble in ether; it sublimes without melting. The *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, crystallises in bright-yellow needles and loses its water at 110°. The *dichromate*, $(C_{11}H_{11}NO)_2,H_2Cr_2O_7$, crystallises in citron-yellow, microscopic needles containing water and is sparingly soluble in cold water. The *picrate*, $C_{11}H_{11}NO,C_6H_3N_3O_7$, crystallises in plates or prisms, turns brown at 200°, melts at 207°, and is completely decomposed at 210°; it is almost insoluble in water, and only sparingly in hot alcohol, benzene, chloroform, and acetone. The yield of hydroxydimethylquinoline, by the method described above, is not more than 20 per cent. of the amidophenol employed. Better results are obtained when a mixture of acetone (1 mol.) and paraldehyde (1 mol.) is saturated with hydrogen chloride, kept for two to three days, and then heated at 100° for six hours with a concentrated hydrochloric acid solution of amidophenol (⅔ mol). (Compare Beyer, Abstr., 1885, 672 and 1246.) The product is purified as described above.

Several sulphonic acids are formed when α-γ-dimethylquinoline is treated with fuming sulphuric acid; when the more sparingly soluble portion of the product is melted with soda, a mixture of substances is obtained, from which, in one experiment, a crystalline product melting above 70° was isolated. (Compare Beyer, Abstr., 1886, 629.) This substance is probably an orthohydroxyquinoline, but it is not identical with the orthohydroxy-derivative described above.

Parahydroxy-α-γ-dimethylquinoline is obtained, together with methane, when paramidophenol is heated with acetone for several days at 170—180°. The product can be purified as described in the case of the ortho-derivative or by means of the crystalline hydrochloride. The yield is only about 12 per cent. of the theoretical quantity, but better results are obtained by using a mixture of acetone and acetaldehyde as described above. It crystallises from alcohol in prisms or small plates, melts at 214° (uncorr.), and boils above 360° with partial decomposition. It is readily soluble in alcohol and acetone, but only sparingly in ether, and almost insoluble in benzene and hot water; it is readily soluble in acids and in alkalis but not in ammonia; the alkaline solutions are precipitated by carbonic anhydride and give coloured precipitates with diazochlorides. The acid alcoholic solution of the colouring matter obtained with β-naphthylamine dyes silk red. Ferric chloride produces a brown coloration in an alcoholic solution of the base, and with bromine an amorphous bromide is obtained. The *hydrochloride*, $C_{11}H_{11}NO,HCl$, crystallises from alcohol in yellowish needles, is readily soluble in water and sublimes when heated. The *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, crystallises in yellow needles and is sparingly soluble in water and alcohol; it loses its water at 110° and decomposes when heated more strongly. The *sulphate*, $(C_{11}H_{11}NO)_2,H_2SO_4$, crystallises from water in colourless needles and is almost insoluble in hot alcohol. The *picrate*, $C_{11}H_{11}NO,C_6H_3N_3O_7$, crystallises in large prisms, melts at 225° with decomposition, is very sparingly soluble in most ordinary solvents and almost insoluble in water. The *dichromate* is not easily obtained in crystals. F. S. K.

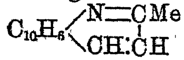
β-Naphthaquinaldine. By F. SEITZ (*Ber.*, **22**, 254—266).—*β-Naphthaquinaldine* crystallises in rhombic plates, melts at 82°, and distils with difficulty with steam. The *hydrochloride*, with 2 mols. H_2O, crystallises in slender, lustrous needles, sparingly soluble in cold water; the *nitrate*, with 1 mol. H_2O, forms slender needles which become pale rose-coloured when exposed to air; the *sulphate*, $C_{14}H_{11}N,H_2SO_4 + 2H_2O$ crystallises in very slender needles, very readily soluble in hot water; the *picrate* forms microscopic needles, melts at 220—221° with decomposition, dissolves very sparingly in boiling water, readily in glacial acetic acid; the *methiodide* crystallises in straw-coloured needles, melts at 241—247° with decomposition, and dissolves readily in boiling water, sparingly in alcohol.

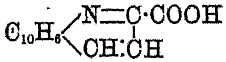
By the action of a mixture of fuming nitric and strong sulphuric acids on β-naphthaquinaldine, four nitro-compounds are formed, two of which are soluble and two insoluble in alcohol.

Dinitro-β-naphthalquinaldine, $C_{14}H_9N(NO_2)_2$, is obtained by crystallising that portion of the product which is soluble in alcohol from glacial acetic acid, and melts at 226—227°. The other soluble compound melts at 250°; it was not further examined.

A second *dinitro-derivative* crystallising in long, yellowish needles, melting at 230°, and the *tetranitro-compound*, $C_{14}H_7N(NO_2)_4$, which crystallises in yellowish-brown, lustrous plates melting at 277°, are insoluble in alcohol, and are separated by crytallisation from glacial acetic acid.

A third *dinitro-derivative* is formed when dry β-naphthaquinaldine nitrate is added to strong sulphuric acid. It crystallises in colourless needles, melts at 205—212°, dissolves readily in benzene and is insoluble in light petroleum.

Carboxyphenylpicolinecarboxylic acid, $COOH{\cdot}C_6H_4{\cdot}C_5NHMe.COOH$ [$C_5N : COOH = 1 : 2$; $C_6H_4 : Me : COOH = 3 : 6 : 2$], is obtained by treating β-naphthaquinaldine (10 grams) suspended in water ($1\frac{1}{2}$ litre) with sulphuric acid (10 grams), and adding to the cold solution potassium permanganate (30 grams), dissolved in water (500 c.c.). Orthophthalic and naphthaquinolinecarboxylic acids are also formed. It crystallises in needles (anhydrous) or in prisms (with 1 mol. H_2O), melts at 201° with violent evolution of carbonic anhydride, and is very sparingly soluble in cold water. *Sodium carboxyphenylpicolinecarboxylate*, $C_{14}H_9Na_2NO_4 + 2H_2O$, forms slender needles, sparingly soluble in boiling alcohol, readily in water; the *potassium salt* is more readily soluble; the *zinc salt* (with $1\frac{1}{2}$ mol. H_2O) is almost insoluble in water; the *copper salt* (with $1\frac{1}{2}$ mol. H_2O) crystallises in microscopic, bluish-green plates. The formation of the acid from β-naphthaquinaldine is analogous to that of β-phenylpyridinedicarboxylic acid from β-naphthaquinoline (Skraup and Cobenzl, Abstr., 1883, 1011). Assuming the acid to have the constitution given above, β-naphthaquinaldine would have the constitution  $C_{10}H_6\!<\!\begin{matrix}N=CMe\\ CH:CH\end{matrix}$ [$CH : N = 1 : 2$].

β-Naphthaquinolinecarboxylic acid,  $C_{10}H_6\!<\!\begin{matrix}N=C{\cdot}COOH\\ CH:CH\end{matrix}$ [$CH : N = 1 : 2$], is obtained as sodium salt by extracting the manganese dioxide formed in the above oxidation experiment with dilute aqueous soda. The acid crystallises from alcohol in very slender, matted needles, which melt with decomposition at 187°; when heated on platinum foil, it evolves irritating vapours. It is almost insoluble in water, sparingly soluble in alcohol and boiling glacial acetic acid. The *sodium salt*, $C_{14}H_8NaNO_2 + 2\frac{1}{2}H_2O$, crystallises in very lustrous scales or needles, sparingly soluble in cold water. The *barium salt* (with 4 mols. H_2O) separates as a flaky precipitate, which becomes crystalline by prolonged boiling; the *copper salt* (with $1\frac{1}{2}$ mol. H_2O) is insoluble in water. The *hydrochloride*, $C_{14}H_9NO_2,HCl$, crystallises in yellow, hair-like needles, and is readily decomposed by water and alcohol; the *platinochloride*, $(C_{14}H_9NO_2)_2,H_2PtCl_6 + 2H_2O$, forms yellow, matted needles, very sparingly soluble in hot dilute hydrochloric acid; water decomposes it readily. The production of the carboxylic acid in the oxidation of β-naphthaquinaldine corresponds with the formation of quinaldic acid from quinaldine (Döbner and v. Miller, Abstr., 1884, 185).

When β-naphthaquinolinecarboxylic acid is heated at 190—200°, β-naphthaquinoline is formed. The platinochloride crystallises with 2 mols. H_2O (not 1 mol. Compare Skraup and Cobenzl, *loc. cit.*, and Lellmann and Schmidt, *Ber.*, **20**, 3156).

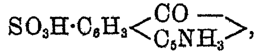
Trichlorhydroxyethylidene-β-naphthaquinaldine, $C_{16}H_{10}NCl_3 + H_2O$, is prepared by v. Miller and Spady's method (Abstr., 1886, 264), by the action of chloral on β-naphthaquinaldine (equal mols.). The reaction takes place with rise of temperature. The whole is then heated for five hours on a water-bath. It crystallises in rhombs, melts at 185°, is insoluble in water, almost insoluble in ether; the best solvent is boiling benzene. N. H. M.

Oxidation of β-Naphthaquinolinesulphonic Acid. By C. Immerheiser (*Ber.*, **22**, 402—411).—The β-naphthaquinolinesulphonic acid was prepared by Skraup's method from pure β-naphthylamine-α-sulphonic acid (Abstr., 1885, 561).

β-Phenylpyridinesulphodicarboxylic acid,

$$SO_3H{\cdot}C_6H_3(COOH){\cdot}C_5NH_3{\cdot}COOH$$

[$C_5N : COOH : SO_3H = 1 : 2 : 6$; $C_6 : COOH = 3 : 2$], is formed by oxidising a 1 per cent. solution of potassium β-naphthaquinolinesulphonate with the calculated quantity of potassium permanganate in ½ per cent. solution. It crystallises from water in transparent, colourless, hard crystals, has an unpleasant, sour taste, and is readily soluble in hot, sparingly soluble in cold water, and almost insoluble in alcohol, ether, benzene, &c. The *potassium*, *barium*, *silver*, and *lead* salts were prepared, but could not be obtained in crystalline form.

β-Pyridinephenyleneketonesulphonic acid,  $SO_3H{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CO\text{—}}{C_5NH_3}{>}$, is prepared by oxidising a solution of potassium β-naphthaquinolinesulphonate in 50 times its weight of 20 per cent. aqueous potash with the calculated quantity of potassium permanganate in ½ per cent. solution. It crystallises from water in scales with 1 mol. H_2O, is readily soluble in hot, and sparingly soluble in cold water, and is almost insoluble in alcohol and ether. The *potassium* salt with 1 mol. H_2O crystallises in long, yellow needles, or in yellow, transparent, monoclinic prisms; the *barium* salt with 2 mols. H_2O crystallises in tufts of yellow needles; the *silver* salt with 1 mol. H_2O crystallises in slender, yellow, hair-like forms; the *lead* salt with 3 mols. H_2O crystallises in lustrous, yellow needles. The *phenylhydrazone*,

$$C_{13}H_7NSO_3{\cdot}N_2HPh,$$

crystallises from acetic acid in small, red needles, decomposes at 295° without melting, and is insoluble in almost all solvents; the *oxime*, $C_{13}H_7NSO_3{:}NOH$, forms yellowish, crystalline flocks, decomposes at 290° without melting, and is sparingly soluble in cold water.

W. P. W.

Condensation of Paranitrobenzaldehyde with Quinaldine. By W. Bulach (*Ber.*, **22**, 285—290).—When a dry ethereal solution of paranitrobenzylidenequinaldine (Abstr., 1887, 976) is treated with bromine, the compound $C_{17}H_{12}N_2O_2Br_2$ is formed; this crystallises from alcohol in lustrous, gold-coloured, matted needles which become brown at 230° and melt at 276°.

Amidobenzylidenequinaldine, $C_{17}H_{14}N_2$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises from weak alcohol in long, gold-coloured needles melting at 172—173°. It is also formed when the base $C_{17}H_{14}N_2O_2$ (*loc. cit.*) is reduced with tin and hydrochloric acid. The *acetyl-derivative*, $C_{19}H_{16}N_2O$, prepared by heating the amido-base with acetic anhydride in a reflux apparatus, crystallises from alcohol in large, tabular, monoclinic crystals which melt at 194° and dissolve readily in alcohol and light petroleum.

Parahydroxybenzylidenequinaldine, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH$, is obtained by diazotising the amido-base and boiling the product with water; it forms brown crystals melting at 255° with decomposition. With β-naphtholdisulphonic acid, the *diazo-compound* yields a dye which colours silk copper-red.

Diquinolylethylene (*ethylenediquinoline*), $C_2H_2(C_9NH_6)_2$, [$CH = 2'$; $CH = 3$], is prepared by heating paramidobenzylidenequinaldine (20 grams) with glycerol (70 grams), sulphuric acid (30 grams), and orthonitrophenol (14 grams) in a reflux apparatus; the heating is discontinued as soon as gas is evolved, as the reaction becomes very violent; it is then heated for one or two hours. The product is diluted with water, saturated with potash and boiled; the resin is dissolved in benzene and boiled with animal charcoal. It crystallises in groups of needles, melts at 146—147°, is sparingly soluble in alcohol and benzene, readily in glacial acetic acid. The *hydriodide* crystallises in brick-red prisms; the *sulphate* in needles. The *dibromide*, $C_2H_2Br_2(C_9NH_6)_2$, crystallises in needles, becomes brown at 280°, and does not melt at 300°; it is readily soluble in hot alcohol. When ethylenediquinoline is heated with hydriodic acid and amorphous phosphorus at 150°, the compound $C_{20}H_{16}N_2$ is formed; this crystallises in lustrous prisms melting at 106·5°.

Ethylenequinolinequinaldine, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_9NH_5Me$ [$CH = 2'$; $CH : Me = 3 : 2'$], is prepared by adding a slight excess of paraldehyde to paramidobenzylidenequinaldine (20 grams) and hydrochloric acid (70 grams) heated at 150°; the reaction soon becomes violent. It is heated for five hours, diluted with water, filtered, and treated with aqueous soda; the resin is dried and repeatedly extracted with alcohol. It is purified by means of the picrate, and the free base crystallised from petroleum (b. p. 100—130°). It crystallises in lustrous, reddish plates, melts at 157·5°, and dissolves very easily in alcohol, ether, and chloroform, less readily in benzene. The salts are mostly sparingly soluble, gelatinous substances. N. H. M.

The Sulphur of Proteïds. By A. Krüger (*Pflüger's Archiv*, **43**, 244—264).—Mulder (*Annalen*, **61**, 121) was the earliest to investigate the condition of the sulphur contained in proteïds, and the fruit of his work was his "Proteïn Theory." He observed that the sulphur is readily separated from the remainder of the proteïd, and the sulphur-free radicle proteïn was supposed to be combined with different amounts of sulphur, so producing different proteïds.

Liebig and others, who showed the inaccuracy of Mulder's work and conclusions, pointed out that warming a proteïd with potash not only removed sulphur but ammonia; and even though the residue gives no further colour with lead salts, it still retains some sulphur.

It is thus possible to speak of two forms of sulphur in proteïd: that which is loosely and that which is firmly combined; and Danilewsky (*Zeit. physiol. Chem.*, **7**, 440) further differentiated the loosely combined sulphur into four varieties according as to whether it was removable with a ½, 2, 5, or 10 per cent. solution respectively of sodium hydroxide. The slowness of the alkali in removing all removable sulphur is analogous to what occurs in cystin (Goldmann and Baumann, Abstr., 1888, 519). The total sulphur (S) and the loosely bound sulphur (L) were estimated in white of egg and fibrin. The results were as follows:—

	S.	L.	S : L.
White of egg	1·66	0·44	4 : 1·06
Fibrin	1·20	0·38	3 : 0·95

There appear to be certain native proteïds which give no blackening with lead and alkali: these contain about 0·8 per cent. or less of sulphur, and seemingly all is in the firmly combined condition. Legumin (sulphur 0·4 per cent., Ritthausen), and caseïn (sulphur 0·8 per cent., Hammarsten) are examples of these.

The proteïd which had been treated with potassium hydroxide for the removal of the loosely combined sulphur was then examined: it was found to be an amorphous peptone-like substance which by saturation with ammonium sulphate was separated into two substances: one precipitable by the salt gave the reactions of an albumose, the other left in solution was a peptone (in Kühne's sense of the word). The percentage composition of these substances was as follows:—

	C.	H.	N.	S.	O.	Ash.
Egg albumin ...	52·98	7·09	15·70	1·6—1·8	22·41	—
Propeptone.....	55·76	6·93	14·46	1·28	21·57	(0·31)
Peptone	48·06	6·73	11·70	0·47	33·04	(2·88)

	C.	H.	N.	S.	O.	Ash.
Fibrin	52·50	6·95	16·57	1·22	22·76	—
Propeptone	55·26	6·75	15·46	0·79	21·74	(0·21)
Peptone	52·58	6·60	14·43	0·47	25·92	(0·85)

In the propeptone in both cases there is a fall in the percentage of nitrogen and sulphur, which is still more marked in the peptone. The sulphur in the propeptone is approximately equal to that in the mother substance which was in the firmly combined condition; and the composition of the two propeptones is nearly the same: thus a substance appears to be formed from different proteïds which has the same composition and which contains all the firmly combined sulphur. The composition of the two peptones is, however, very different, and they are probably produced from the propeptones by further hydrating action; the loss of sulphur is probably due to the formation of another sulphur-containing organic compound that escaped detection; sulphates are not formed.

The concluding portion of the paper is devoted to a theoretical consideration of the probable way in which the sulphur is actually present in the proteïd. Tables are given of the chief sulphur-containing substances known, and as to whether or not they are blackened by lead and alkali. The number of those that are not blackened is much smaller than those that are. The firmly bound sulphur is compared to that in mercaptan, thioether, and sulphinic compounds, and the loosely combined sulphur to that in thio-acids, cystin, and compounds in which either the group ⁝C⁚S or ⁝C·S·S·C⁚ is present.

W. D. H.

Myosin. By R. H. Chittenden and G. W. Cummins (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 115—138).—Ammonium chloride solutions were found the most efficacious in extracting myosin from flesh. The salt was removed by dialysis, and the myosin obtained in a jelly-like condition. This appears to be, as pointed out by Halliburton, a genuine recoagulation rather than a simple precipitation (Abstr., 1887, 984). A large number of preparations were made from different animals, and the results of elementary analysis show a very close agreement. With regard to the temperature of heat-coagulation of this proteïd, the results differ slightly in different animals, and also differ, to a slight extent, from those obtained by Halliburton: this is, no doubt, to be explained by the character of the saline solution used, Halliburton having used a magnesium or sodium sulphate solution. The general results justify the assumption that myosin as it occurs throughout the animal kingdom is a single chemical compound formed, as suggested by Halliburton, by the interaction of one or more myosinogens and a ferment.

W. D. H.

Caseoses, Caseïn Dyspeptone, and Caseïn-Peptone. By R. H. Chittenden and others (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 66—105).—This paper gives fuller and further details than were before published (Abstr., 1888, 76) of the properties and elementary composition of the peptone formed from caseïn, of the intermediate products (caseoses), and of an insoluble bye-product formed during the earlier stages of the digestive process (caseïn-dyspeptone).

W. D. H.

Reduced Hæmoglobin. By L. Hermann (*Pflüger's Archiv*, **43**, 235).—The spectrum of reduced hæmoglobin is generally described as showing only one absorption-band. But if this band be examined carefully (whether the reduction has been produced by Stokes' reagent, ammonium sulphide, or a stream of hydrogen), it will be seen to consist of two: a wide dominant band, and, separated from it by a less brightly illuminated narrow space, a narrow band almost coincident with the D line. W. D. H.

Reducing Action of Indigo-white on Oxyhæmoglobin. By E. Lambling (*Compt. rend. Soc. Biol.*, [2], 5, 394—396).—Schützenberger (*Bull. Soc. Chim.*, 1873, 150) used indigo-white to remove the oxygen from oxyhæmoglobin, and obtained by that method a result higher by 4—5 c.c. of oxygen per 100 c.c. of blood than by the method of extracting the gas by the mercurial air-pump. This difference increases with the length of time employed in the extraction of the gas by the air-pump, and it is easily explicable on the theory that the loss of the oxygen is due to its combination with the still living tissue elements in the blood, especially as the temperature at which the operation is performed is 40—50°, and, perhaps, also to the formation of methæmoglobin. Hoppe-Seyler (*Physiol. Chem.*, 451), however, considers that the reduction of oxyhæmoglobin does not stop at hæmoglobin, but goes on to hæmochromogen when indigo-white is employed: the experiments on which this opinion is based are, however, not stated. In the present research, spectroscopic observations were made on the effect of the prolonged action of a stream of hydrogen and of indigo-white respectively on solutions of oxyhæmoglobin obtained by diluting blood with water. In neither case did the bands of hæmochromogen appear, but the reduction always stopped when hæmoglobin was formed. W. D. H.

Pigments of the Urine. By C. A. MACMUNN (*J. Physiol.*, **10**, 71—121).—A full account, with plates of absorption-spectra and measurement of bands, of experiments of which an account has already appeared (Abstr., 1888, 614). W. D. H.

Physiological Chemistry.

Gases of Peptone Blood. By LAHOUSSE (*Archiv f. Anat. u. Physiol., Physiol. Abth.*, 1889, 77—82).—As compared with normal blood, the amount of carbonic anhydride in "peptone-blood" is greatly diminished, approximately to about half the normal; on the other hand, the amount of oxygen is slightly increased, namely, from 15—16 to 16—17 per cent. The experiments were performed on dogs. "Peptone blood" does not clot, and in connection with the diminution of carbonic anhydride it is interesting to note the well-known fact, that passing a stream of that gas through the blood or through "peptone plasma" will cause it to coagulate. The temperature of the body first rises slightly during "peptone narcosis," and then returns to the normal, or rather below it. W. D. H.

Amount of Hæmoglobin in the Blood during Inanition. By S. GROLL and L. HERMANN (*Pflüger's Archiv*, **43**, 239—244).—The question investigated was the relation of hæmoglobin to the total solids of the blood during starvation: the experiments were carried out on rabbits, cats, and a dog:—

If p = total solids of the blood per cent.,
h = amount of hæmoglobin, as measured by the graduations on Fleischl's hæmometer;

then $q = h/p$ is the colour quotient, which was the object of investigation. The results, which are given in tabular form in 16 experiments, show that during a state of hunger, hæmoglobin is less quickly used up than the other solid constituents of the blood. W. D. H.

Production of the Proteïds of the Blood. By S. Torup (*Compt. rend. Soc. Biol.* [2], 5, 413—416).—It is well known that peptone is absent from the blood even during the periods of most active digestion. During or immediately after absorption, the peptones are transformed either into the proteïds of the blood (fibrinogen, serum-globulin, serum-albumin), or into certain nitrogenous non-proteïd substances. The former hypothesis is that most generally held by physiologists. The present experiments bearing on this point are merely preliminary to a more detailed investigation not yet completed. They were three in number, all made on dogs. Blood was removed from the animal at three different periods extending over a week, during which time the animal received no food. The blood was analysed, and in order to prevent any alteration in the volume and pressure of the blood, a solution of sodium chloride (0·7 per cent.) was injected in amount equal to that of the blood removed.

In all three experiments, the results were perfectly concordant: one may therefore serve as an example of the whole.

	Dates.		
	2nd Feb.	4th Feb.	8th Feb.
Weight of dog	11·5 kilos.	10·85 kilos.	10·5 kilos.
Percentage of proteïds in blood	13·7	14 9	15·5
Percentage of globulin in serum	1·4	1·8	2·0
Percentage of albumin in serum	2·7	2·9	3 1
Percentage of fibrin in blood	0·18	0·22	0·41
Red corpuscles per cubic millimeter of blood	3450000	3750000	4540000
Quantity of blood in c.c.	897	—	863

The conclusions drawn are as follow:—

1. If a certain quantity of the blood is removed, and the animal is left in a state of inanition, an increase of the proteïd constituents of the blood takes place. This increase is not only relative, but absolute.

2. The increase is chiefly due to the increase in the number of the red corpuscles.

3. The increase of the proteïds of the serum is less marked, but is sufficiently manifest.

4. The increase of fibrin is considerable when the small quantity existing in normal blood is taken into account.

5. In these experiments, the increase in these constituents could not have been due to peptones absorbed from the alimentary canal.

W. D. H.

Influence of Saline Materials on Gaseous Metabolism in Man. By A. LOEWY (*Pflüger's Archiv*, **43**, 515—532).—v. Mering and Zuntz (*Pflüger's Archiv*, **15**, 634; **32**, 173) found that when nutritive materials, either nitrogenous or non-nitrogenous, were introduced into the circulation, the oxygen taken in remained unaltered; the carbonic anhydride exhaled was increased owing to the burning off of the substance given. When the material was introduced into the stomach, the rise of oxygen used would be quite well explained by the increased work of the digestion apparatus. Voit (*Zeit. Biol.*, **14**) and Rubner (*ibid.*, **19**), on the contrary, did not find any increase in the oxygen used through activity of the alimentary tract. The work of other observers in the same direction is also quoted, and the subject is of some practical interest, as therapeutically the cures of Carlsbad, Marienbad, &c., consist in increasing the activity of the intestinal tract by the administration of saline purges. These experiments were therefore undertaken. The rabbit was the animal, and Glauber's salts the saline purge selected. Further experiments were performed on men. Such a salt can itself produce no alteration in gaseous interchange due to its own combustion.

The details of the method employed are given, and the results show in tabular form, the volume of air breathed, oxygen used, carbonic anhydride given out per minute and per cent., and, lastly, the respiratory quotient. This is given first for the normal state, then for the same person under the influence of sodium sulphate. The result constantly obtained was an increase of the gaseous exchanges in the lungs during the latter period: not only is the carbonic anhydride exhaled increased, but the oxygen taken in is increased also. Thus the results are in accord with those of v. Mering and Zuntz.

The increased metabolism appears to be due to the activity both of the muscular tissue of the intestine and of the glands, but probably the former is the more important factor concerned. W. D. H.

Digestion in Mules. By A. SANSON (*Compt. rend. Soc. Biol.* [2], **5**, 316—318).—From experiments on a horse, mule, and ass, the conclusion is drawn that the power of digesting proteïds is greater in the mule than in the horse, and that this power is inherited in the mule from the ass. W. D. H.

Influence of certain Therapeutic Agents on Amylolytic and Proteolytic Digestion. By R. H. CHITTENDEN and C. W. STEWART (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 60—65).—The methods employed were similar to those used in previous experiments of the kind (Abstr., 1888, 78).

Antipyrin in large doses has a slight inhibitory influence on amylolytic digestion; antifebrin or acetanilide is comparatively insoluble in water, and so large percentages could not be employed; such as were used, however, had little or no influence on amylolytic digestion. Ethylurethane slightly stimulates amylolytic action. Paraldehyde showed a very strong inhibitory power on the same kind of digestion, and this was even more marked in the case of thallin sulphate. Caffeïne and theïne in large doses produce a slight diminution in the amount of starch converted.

The action of the same drugs on gastric digestion was then investigated. Antipyrin has a decided inhibitory influence, and when present to the extent of 3 per cent. practically stops all digestive action. Antifebrin, caffeïne, and theïne have a similar inhibitory action. The retarding action of urethane is very slight, and paraldehyde and thallin sulphate have a decided stimulating action on the pepsin ferment.

On the proteolytic action of trypsin two substances only were tested, namely, antifebrin and paraldehyde; both showed a marked inhibitory action. W. D. H.

Influence of Urethane, Paraldehyde, Antipyrin, and Antifebrin on Proteïd Metabolism. By R. H. Chittenden and others (*Studies from Lab. Physiol. Chem., Yale Univ.*, 3, 39—59; and *Zeit. Biol.*, 25, 496—512).—The experiments with ethylurethane were conducted wholly upon the person of a healthy man. The experiment extended over six weeks, during which time a fixed diet was taken. Body equilibrium being established, the urine was analysed daily, first for a period without, and then for a second period with, the administration of the drug. The experiment was repeated, and the results, of which full details are given, were as follows: the drug has a decided diuretic action, most noticeable on the second day after the drug is taken; the excretion of nitrogen is decidedly below the normal, even after a dose of 5—10 grains. The phosphorus excreted seems to be slightly increased with small doses, diminished with large doses. The excretion of sulphur runs parallel with that of nitrogen. No hypnotic action was produced with the doses taken.

The experiments with paraldehyde were similarly conducted, not, however, on a man, but on a dog; the animal remained perfectly well during the experiment, exhibiting neither nausea nor sleepiness. The drug was found to produce practically no influence on proteïd metabolism.

The action of antipyrin was investigated by means of experiments on a healthy man. Urea and uric acid were estimated separately, and were found to be diminished in amount by the administration of the drug. Antifebrin (also investigated by experiments on man) slightly increases the excretion of urea, but hinders that of uric acid.

W. D. H.

Gastric Juice of Crayfish. By Stamati (*Compt. rend. Soc. Biol.* [2], 5, 16—17).—By means of a gastric fistula, the gastric juice can be easily collected from the crayfish. This secretion is yellowish, somewhat opalescent, and always alkaline. It digests fibrin rapidly, forming peptones, which give the ordinary reactions; it also transforms starch into sugar. It appears also that fats are emulsified and fatty acids liberated. W. D. H.

Secretion of Saliva. By J. N. Langley and H. M. Fletcher (*Proc. Roy. Soc.*, 45, 16—18).—The author's confirm Heidenhain's law that the precentage of salt in saliva increases with the rate of secretion. The following facts were also observed:—Stimulating the sympathetic gives saliva containing a larger percentage of salt than that obtained by stimulating the chorda. Dyspnœa increases the percentage of salts and of organic substances, as do bleeding and clamping the carotid. Injection of sodium chloride, 0·2—0·6 per cent., increases the secretion of saliva but decreases the percentage of salts. Sodium carbonate also increases the secretion. Injection of strong salt solution increases the percentage of salts and of organic substances; this being probably due to a decrease in the blood flow through the gland. The general results of the investigation are that the secretion of water, salts, and organic substances is determined by the strength of the stimulus, the character of the blood, and the amount supplied to the gland, and is not due to the stimulation of any particular nerve.

H. K. T.

Aqueous Humor. By A. GRUENHAGEN (*Pflüger's Archiv*, **43**, 377—384).—The substance in the aqueous humor that reduces Fehling's solution, and which was described by Kühn (this vol., p. 177) as sugar, cannot be sugar, as it does not ferment with yeast. The dextrorotatory action of the humor is apparently due to sarcolactic acid, together with a "still unknown dextrorotatory substance" with which it is mixed. The substance which causes the reduction of alkaline solutions of copper hydroxide is precipitable by lead acetate and ammonia; it is not precipitated by potassic-mercuric iodide, it is optically inactive, and seems not to be a carbohydrate.

W. D. H.

Reducing Substances in Urine. By HAGEMANN (*Pflüger's Archiv*, **43**, 501—514).—It has long been known that sugar is not the only substance occurring in urine which reduces alkaline solutions of cupric hydroxide. Uric acid and creatinine act similarly; but more important still are the compounds of glycuronic acid that have been more recently described. This substance occurs in normal and in certain pathological conditions, and is much increased by the administration of camphor, chloral hydrate, phenol, benzoic acid, and other drugs. The existence of this acid in urine and its reducing action similar to that of sugar, renders a very careful examination of the urine necessary in suspected cases of diabetes.

Various practical difficulties in the use of Fehling's solution are pointed out; the most important of these appears to be the difficulty of finding a trustworthy end reaction; it was, however, found that the small addition of calcium chloride prevents the mechanical suspension of cuprous oxide in the solution, and that a filtrate free from copper can be obtained when all the cupric oxide has been reduced (Flückiger, *Zeit. physiol. Chem.*, **9**, 335). It is, however, necessary in urine to test the first two drops of the filtrate; by the time the third drop comes through, oxidation of the cuprous oxide has taken place, and cupric oxide is in solution. Such rapid reoxidation does not occur in solutions of pure dextrose. But by quick filtration, and testing the two first drops as just stated, approximately equal results are obtained by titration as by Allihn's method of weighing. Using always the same amount of calcium chloride solution, it was found necessary to make a certain small addition to the amount of sugar as obtained.

In horse's urine (the animal being fed on an average diet, of which the details are given) no sugar was found, but on the average 0·004886 per cent. of reducing substances, or about 14 grams per diem. There were merely traces of uric acid and creatinine: the greater amount of the reducing substance is probably glycuronic acid. It is considered probable that glycuronic acid is derived from certain changes in proteïds, especially those occurring in the intestine of the nature of putrefaction. In animals that take large quantities of proteïd food, the amount of glycuronic acid in the urine is greater than is the case in the horse. W. D. H.

Rennet in Human Urine. By F. HELWES (*Pflüger's Archiv*, **43**, 384—396).—Rennet ferment is pretty regularly present in normal human urine, but often the amount present is exceedingly small. The small amount is what one would expect, when the fact is remembered that alkalis destroy the ferment more easily than they destroy pepsin (Hammarsten). W. D. H.

Nitrogenous Constituents of Urine. By K. BOHLAND (*Pflüger's Archiv*, **43**, 30—70).—Pflüger and Bohland found that 13·4 per cent. of the nitrogen of the urine was not combined as urea. The present research relates to this point, the amount of ammonia and ammonium salts being also determined. The total nitrogen was first estimated. Urea was then estimated by Bunsen's method after the removal of the extractives precipitable by phosphotungstic acid. The amount of nitrogen in this precipitate was estimated, and also the ammonia by Schlösing's method, both in the fresh urine and in the urine rendered alkaline after treatment with phosphotungstic acid. These processes were carried out in 13 series of urines, many of them from patients suffering from fever. The results and details of each analysis are given in full and in tabular form. The mean result was as follows:—15·54 per cent. of the nitrogen is not combined as urea: of this 0·065 exists as preformed ammonia; the nitrogen in the precipitate produced by phosphotungstic acid was 6·51 per cent. of the whole; 4·4 per cent. of nitrogen from unknown substances was found in the urine from which the precipitate produced by phosphotungstic acid had been filtered off. W. D. H.

Chemical Composition of a Kidney which had undergone Waxy Degeneration. By E. LAMBLING (*Compt. rend. Soc. Biol.* [2], **5**, 51—52).—The method of analysis employed was Hoppe-Seyler's (Gottwalt, *Zeit. physiol. Chem.*, **4**, 437). The blood was first removed by a stream of saline solution: the kidney was then reduced to a fine state of subdivision: the substances soluble in water, and in solutions of sodium carbonate, and sodium chloride removed successively. The residue was heated with water in a sealed tube at 120° to convert the collagen of the connective tissue into gelatin. The albuminoïd (amyloïd) substance was isolated in another portion of the renal tissue by the method of Friedreich and Kekulé

(*Virchow's Archiv*, **16**, 58), and then purified by Kühne's method (*Maly's Jahresber.*, **3**, 31) by artificial digestion with gastric juice and subsequent treatment with baryta-water. The percentage results compared with those of Gottwalt in healthy kidneys are as follows :—

	Healthy kidney.	Waxy kidney.
Albumin	1·116—1·394	0·792
Globulin	8·633—9·225	5·553
Other proteïds......	1·436—1·598	0·485
Gelatin............	0·996—1·849	2·685
Albuminoïd substance	—	0·992

There is thus a diminution in the proteïds present, as compared with healthy kidneys; but the percentage of albuminoïd material appears very low, considering the very advanced state of degeneration revealed by the microscope. It is considered possible that the transparent, swollen appearance of the organ may be in part due to the formation of a substance of the nature of the hyalins described by Krukenberg (Abstr., 1886, 481). W. D. H.

Influence of Arsenic and Antimony on the Glycogenic Function and Fatty Degeneration of the Liver. By R. H. CHITTENDEN and J. A. BLAKE (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 106—114).—From a few experiments on rabbits and fowls, it would appear that small doses of antimonious oxide long continued tend to increase the body-weight, and particularly the weight of the liver. Further, the increase in liver-weight is accompanied by an increased percentage of fat and a slight increase of glycogen in the liver. With corresponding doses of arsenious oxide, on the other hand, the results would indicate a diminution in body-weight, also a diminution in the weight of the liver and amount of liver glycogen. In some cases there is, however, pronounced fatty degeneration of the liver.

W. D. H.

Physiological Action of Uranium Salts. By R. H. CHITTENDEN and A. LAMBERT (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 1—18, and *Zeit. Biol.*, **25**, 513—532).—Previous experiments (Abstr., 1888, 78) have shown that uranium salts have a marked inhibitory influence on the activity of the digestive ferments; the present investigation relates to (1) the influence of uranium salts on proteïd metabolism; (2) their toxic action; and (3) the influence of uranium in the production of glycosuria.

The experiments on proteïd metabolism were conducted on dogs and rabbits; the animal under investigation was confined in a suitable cage, and fed during an experiment on a constant diet of known composition. When nitrogenous equilibrium was established, the 24 hours' urine was analysed for a number of consecutive days; uranyl nitrate was then administered with the food in gradually increasing quantities for a number of days, and the urine again examined. The points noted in the urine were reaction, volume, specific gravity, amounts of nitrogen, sulphur, and phosphorus.

In these and other cases, the presence or absence of albumin or sugar in the urine was also noted, and if present, the amount was estimated: albumin by boiling with acetic acid, and weighing the coagulum thus produced, sugar by Allihn's gravimetric method.

Experiments on the toxic action of uranium salts were confined wholly to the action of pure uranyl nitrate on rabbits.

The results obtained may be thus summarised:—Uranium is an irritant poison, and like other metallic irritants produces gastro-intestinal irritation of more or less intensity. But it is not in any sense a rapid poison, and the injection of a fatal dose is not followed by any noticeable effects for some time. The action of a small amount (0·15 gram) seems to be as rapid and pronounced as that of a larger quantity (1 gram). The first noticeable symptom is muscular weakness; the salt checks digestion, but apparently increases to a slight extent proteïd metabolism: it increases the output of carbonic anhydride, raises the body temperature, and finally leads to emaciation.

In the kidney, a condition of acute nephritis and destruction of the renal tissue is found like that produced in poisoning by arsenic, mercury, and phosphorus. Albuminuria is severe and constant. With small doses, the volume of urine is increased, but when toxic action is pronounced there may be partial or even complete suppression of that secretion. The production of glycosuria generally occurs after that of albuminuria, but it is a very constant and characteristic symptom. Salkowski has shown that mercury, and H. C. Wood (*Therapeutics*, p. 110) that phosphorus, will occasionally produce diabetes when given in toxic doses. The urine, in cases of uranium poisoning, invariably contains a large amount of crystallised calcium oxalate. In chronic poisoning by uranium, the nervous symptoms (loss of sight and of co-ordinating power) sometimes predominate.
W. D. H.

Relative Absorption of Nickel and Cobalt Salts. By R. H. CHITTENDEN and C. NORRIS (*Studies from Lab. Physiol. Chem., Yale Univ.*, 3, 148—157).—Doses of these salts were given to rabbits, the symptoms observed, and after death the relative quantities of the metal in different organs estimated. The soluble nickel and cobalt salts are possessed of decidedly toxic properties, but their poisonous action is slow and manifested only when large doses are administered. The two salts act very much alike. Both cause death by stopping the heart, and also produce enteritis and interference with digestive processes. Unlike uranium, the metals have no action on the liver or kidney. Both salts, but especially those of cobalt, produce paralysis of the extremities. The salts form in great measure insoluble compounds with the proteïds of the food, and are excreted with the fæces; part enters the circulation, and is rapidly distributed to all parts of the body, and is eliminated ultimately in the urine. The body temperature is raised, and the peripheral cutaneous vessels are constricted.

Among the organs, the spinal cord and brain stand first in their power of picking up and storing the metal; this is also the case with arsenic. As in the case of arsenic also, the muscular tissues retain a larger percentage of the metals than the liver or kidneys; the muscular tissue of the back acts in this way to a greater extent than that of the leg; this fact is not explicable on the ground of difference in vascularity. The lungs and heart also contain high percentages of the metal. W. D. H.

Physiological Action of Antharobin and Chrysarobin. By T. WEYL (*Pflüger's Archiv*, **43**, 367—377; compare Liebermann, Abstr., 1888, 518).—From experiments on man and on healthy animals, the following conclusions are drawn:—

Chrysarobin acts poisonously in very small doses, producing vomiting, diarrhœa, and albuminuria; antharobin, on the other hand, applied by inunction, subcutaneous injection, or by the stomach, is free from poisonous action. It is therefore preferable, when practicable, to use antharobin instead of chrysarobin therapeutically.

Antharobin appears in the urine for the most part unchanged; a small portion is oxidised to form alizarin. The amount of alizarin increases when the urine is left for a time. Any certain proof that chrysarobin passes into the condition of chrysophanic acid in the organism is not yet forthcoming. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Disengagement of Carbonic Anhydride with Anaerobic Yeast. By GRÉHANT and QUINQUAUD (*Compt. rend. Soc. Biol.* [2], **5**, 400).—Yeast suspended in distilled water, and placed in the vacuum of a mercurial air-pump, gives off carbonic anhydride in large quantities, but no oxygen. It thus contains carbon and oxygen in its own substance. The disengagement of gas occurs most readily at a temperature of 40°. After the action is allowed to go on for more than 24 hours, small quantities of hydrogen, and even of nitrogen, are also formed, doubtless from the occurrence of putrefaction in the proteid substances contained in the yeast cells. When this decomposition has occurred, the yeast loses its property of making sugar ferment. W. D. H.

Chemical Composition of the Bacillus from Erythema Nodosum. By V. BOVET (*Monatsh.*, **9**, 1154—1157).—Seven litres of recently sterilised beef extract, containing 5 per cent. of glycerol and 1 per cent. of peptone, were impregnated with Demme's pure culture (*Fortschritt. Med.*, April, 1888), and allowed to remain at 37—38° for eight days, when the fluid commenced to clear, and a thick layer of bacteria collected at the bottom of the containing vessel. The air-dried bacteria weighed 4·148 grams, and lost 2·9532 grams on drying at 110°, the residue having the following composition:—

Extracted by alcohol	8·97 per cent.
Extracted by ether	1·99 „
Ash (PO_4, Cl, K, Ca, and Mg)	7·5 „
Albuminoïds	64·2 „
Cellulose and other non-nitrogenous substances	17·34 „

The alcoholic extract produced no toxicological action when injected under the skin of a guinea-pig. G. T. M.

Reserve Materials, especially Tannin, contained in Evergreen Leaves. By E. SCHULTZ (? SCHULZE) (*Ann. Agronom.*, **14**, 525—526).—The author's microchemical observations support the view of Sachs and Haberlandt that the persistent leaves of evergreens serve as storehouses of reserve material in winter; at any rate, that is true as regards the Gymnosperms and the majority of Dicotyledons. The leaves of conifers contain tannin, sometimes alone, sometimes associated with starch and oil; when oil is present, it is generally in cells free from starch. The author regards tannin as a reserve material. J. M. H. M.

The Reserve Substances in Evergreen Leaves, with Special Reference to Tannin. By E. SCHULZE (*Bied. Centr.*, **18**, 137).—Evergreen leaves contain starch, fatty oil, and tannin as reserve substances. The leaves either contain two reserve substances simultaneously at the period of rest or growth, in which case they are present as starch and tannin or fatty oil and tannin, or else there is only one substance, tannin, present. When starch and tannin occur together, the latter is generally more in the elements of the assimilation tissue, and in the parenchyma sheaths of the fibrovascular bundles in the lamina, whilst the starch is more in the midrib and its immediate vicinity. Tannin and starch only rarely occur simultaneously in the same cells. When the cells are rich in starch, they contain a smaller amount of tannin, and *vice versâ.* In the case of leaves containing fatty oil and tannin, the cells which contain the oil are free from tannin. In most evergreen leaves in which tannin alone is present as reserve substance, it is equally distributed over the elements of the leaf sheath and the midrib. N. H. M.

Transformation of Force and of Material in Plant Respiration. By H. RODEWALD (*Ann. Agronom.*, **14**, 526; compare the author's previous researches, Abstr., 1878, 979).—Experiments with the thickened horny stem of the kohl rabi, arranged in such a manner as to allow simultaneous determinations of the heat evolved, the carbonic anhydride emitted, and the oxygen absorbed, show the ratio CO_2/O to be 1·061. The greater part of the combustible substance is therefore carbohydrate, and must be glucose, since starch and the dextrins are not found in this vegetable. Glucose furnishes 4·95 cal. by combustion for each c.c. of carbonic anhydride formed; in the experiments each c.c. of carbonic anhydride found corresponded to 4·57 cal., or each c.c. of oxygen absorbed to 4·46 cal. Perhaps a small quantity of a more oxygenised substance was burned with the glucose in the plant. J. M. H. M.

Absence of Nitric Acid in Wine-must. By E. POLLAK (*Chem. Zeit.*, **12**, 1623—1624).—In a previous communication, the author stated that he had detected nitric acid in certain musts, he now finds this must have been due to impurities derived from the butts, inasmuch as nitric acid was not detected in the following year either in musts of similar origin, or in the grape-juice. D. A. L.

Absence of Nitrates in Forest Trees. By E. EBERMAYER (*Ann. Agronom.*, **14**, 571).—The soil of forests, and the drainage water of such soil, contain no nitrates, hence their absence from the trees. If trees are grown in a well-manured field, or in garden soil, their organs always give the nitrate reaction with diphenylamine and sulphuric acid. J. M. H. M.

Laurel-nut Oil. By D. HOOPER (*Pharm. J. Trans.* [3], **19**, 525).—The oil examined was derived from *Calophyllum inophyllum*, which occurs throughout India and Malaya. It is thick, greenish-yellow, of fragrant odour, and of bitter taste. It congeals at 19°, and is quite solid at 16°, at which temperature its sp. gr. is 0·9315. The free acid corresponds with 1·89 parts of potash per 100 of oil; its saponification requires 19·6 per cent. of potash. It yields to alcohol 7 per cent. of a peculiar green extract, and the general results place it in close relationship with cotton-seed oil, and in an intermediate position between drying and non-drying oils. R. R.

Quince and Salep Mucus. By R. GANS and B. TOLLENS (*Annalen*, **249**, 245—257).—The syrup from the quince yields furfuraldehyde on distillation with dilute sulphuric acid, indicating the presence of arabinose or xylose, but no crystalline carbohydrate was isolated. The syrup contains neither dextrose nor galactose, as neither saccharic nor mucic acids were formed on oxidation. No furfuraldehyde is obtained by distilling salep syrup with dilute acids. On oxidation, salep yields saccharic acid but no mucic acid. With phenylhydrazine and sodium acetate, the syrup forms a precipitate which can be separated by repeated recrystallisation into the phenylhydrazine compounds of dextrose and mannose. These results show that the syrup contains dextrose and mannose, but neither galactose nor arabinose. W. C. W.

Tannic Acid in Caucasian Wild Sumach. By A. LIDOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 607—608).—Tannic acid was determined by Fleck's method. The leaves and stalks of *Rhus cotinus* were found to contain 13·26 per cent. of tannic acid, the leaves of *Rhus coriaria* 15·31 per cent., and the stalks 3·40 per cent. of tannic and 11 per cent. of gallic acid. B. B.

Field Experiments at Grignon in 1888. By P. P. DEHÉRAIN (*Ann. Agronom.*, **14**, 529—554).—*Wheat.*—The experiments relate to attempts to introduce the "Square-head" wheat into cultivation in France to replace the Bordeaux wheat, the former having been found by the author to bear much heavier manuring without liability to become laid, and to give in consequence much heavier crops than the latter. The experiments of 1887 and 1888 have brought out a difference between the two stocks of Square-head seed in the author's possession, leading him to suppose that one strain may be found better adapted than another to support the greater heat of central and southern France, and may be still further acclimatised by cultivation. If Square-head, or other good yielding wheat, is grown after clover on light land, an application of manure is found beneficial; with Bordeaux wheat, on the contrary, this practice would result in the crop being laid. The summers of 1887 and 1888 were opposite in character: the former hot and dry, the latter cold and wet. The result was that in 1887 the starch in the grain increased rapidly in the week or two preceding harvest, owing to the physiological activity of the leaves; in 1888 the starch remained stationary during the same period, but there was a rapid increase in the albuminoïd and ash, the roots being able to find and carry up into the plant abundance of nitrogen compounds and minerals.

Oats.—Grown after sugar-beet in the four-course rotation, the two most prolific varieties hitherto tried by the author ("l'avoine des salines," commonly grown in the north, and Vilmorin's new variety, "l'avoine géante à grappes,") gave in 1888 mean yields of 34·6 and 33·6 metric quintals of grain, and 67·0 and 55·7 metric quintals of straw per hectare.

Forage Crops.—In certain cases, especially where there is a great demand for green stuff to be consumed on the farm, as in dairying, it may be advantageous, in climates which admit of it, to substitute for the clover which usually follows the oat crop, *T. incarnatum* and forage maize, the latter being sown at the end of June, after removal of the trifolium and a good dunging.

Sugar-beet.—The results of the previous year's experiments are confirmed. Farmers having once purchased an improved strain of seed will find it economical to grow their own seed from well-shaped, medium sized roots of 300—400 grams weight. On light lands, farmyard manure is indispensable. J. M. H. M.

Calcium in Soils. By P. DE MONDESIR (*Compt. rend.*, **108**, 185—187).—Almost all soils, and even those of the most acid character, contain a notable quantity of calcium which does not exist in the form of calcium carbonate as is usually assumed, but is present in combination with other constituents of the soil. Calcium carbonate, as a matter of fact, is absent from a large number of soils, and the sulphate, phosphate, and nitrate are present in very minute quantity, if at all. It follows, therefore, that this compound of calcium with the humoid matter is the most important form in which calcium is present in soils.

The author insists on the importance of carefully distinguishing the different forms in which calcium occurs in any soil, and of not making the usual but erroneous assumption that it occurs mainly in the form of carbonate. C. H. B.

Humous Compounds in Soil. By C. G. EGGERTZ (*Bied. Centr.*, 1889, 75—80).—The author considers that humic and ulmic acids, as generally produced from carbohydrates, are not natural, but laboratory products, whilst crenic and apocrenic acids are genuine compounds, whose properties are but little known. The real ammonium humates are completely soluble in water, whereas the artificially prepared substances are insoluble after drying. If ammonium humate is heated at 110°, or if dry humic acid is exposed to ammonia, a highly nitrogenous compound is produced, in which the nitrogen is intimately combined with the complex organic molecule. Repeated solution in alkali and precipitation by acid results in a partial decomposition, but the whole of the nitrogen is not separated. Sulphur and iron, which appear in natural humous compounds, are not present as sulphates or salt of iron, but are to be considered as combined with the organic compounds.

Humous soils owe their absorptive capacity for phosphates to the phosphorus which is combined in them, for if this phosphorus is removed by acids, &c., the humous compounds can no longer absorb phosphates. The decomposition which humic acids appear to suffer by repeated solution and precipitation, results in the formation of new compounds, which are more soluble in acids than the original substance. Silicic acid appears to be present in peaty soils in the form of ammonium silicate. The amount of matter dissolved out by 4 per cent. acid from a soil, more than represents the potential plant nutriment, as the natural acid which renders this nutriment soluble is much feebler than the acids usually employed in analysis. Ammonia acts on a soil by decomposing the humous compounds; lime acts beneficially by setting free ammonia, which again reacts on humates. E. W. P.

Analysis of Tobacco "Screenings." By L. P. BROWN (*Amer. Chem. J.*, **11**, 37—38).—This material consists of small fragments of stems and leaves, which, with the dust, are sifted from the tobacco during manufacture. It is not unfrequently applied as a top dressing to grass, &c.

Water (loss at 100°)	10·27
Total mineral matter	43·40
Organic matter (difference)	46·33

In the organic matter—

Nicotine	0·36
Albuminoïds and nitrates	6·96
Total nitrogen equal to ammonia	1·48

Constituents of the Ash.

In 100 parts of screenings.

K_2O.	Na_2O.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	SiO_2.	P_2O_5.
1·187	0·506	2·796	0·346	0·192	0·212	33·760	0·296

SO_3.	Cl.	SiO_2 (soluble).	Total.
0·483	0·451	0·907	41·136

In 100 parts of ash.

K_2O.	Na_2O.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	SiO_2.	P_2O_5.	SO_3.
2·89	1·23	6·81	0·84	0·47	0·52	82·32	0·72	1·14

Cl.	SiO_2 (soluble).	Deduct O = Cl.	Total.
1·10	2·21	0·25	100·00

J. W. L.

Analytical Chemistry.

Kaolin Balls for Gas Analysis by Bunsen's Method. By N. A. Bunge (*J. Russ. Chem. Soc.*, 1888, **20**, 694—701).—In gas analysis, instead of using balls made of papier-maché or coke soaked with various liquids such as alkaline pyrogallol solution, sulphuric acid, &c., for the absoption of certain gases, the author recommends a mixture of kaolin and soot; this is made into a paste and formed into balls of about 10 mm. in diameter; the ball is then fastened at the end of a hooked, thick platinum wire, and compressed in an ordinary bullet mould (or as the author recommends, in a mould made of plaster of Paris). After taking the ball out of the mould, it is cleaned, smoothed, dried, and heated to redness by a Bunsen burner. In this way, a coherent, porous ball is obtained, which breaks with difficulty and may be used over and over again. The best proportions are 3 parts of kaolin to 1 part of soot. [A thick solution of honey may be added with advantage.—B. B.] In order to saturate the ball with pyrogallol solution, a thick test-tube is nearly filled with mercury, and the remaining space with a solution of 1 gram of pyrogallol in 2 c.c. of water. After adding 1·3 grams of solid potash, the test-tube is inverted over mercury. To use it, the ball is brought up from below into the solution, and as soon as no more bubbles of gas are observed to escape, it is brought into the gas to be analysed, keeping it under the mercury all the time, and not allowing it to come even for one moment into contact with air. In order to avoid the tedious process of transferring gases, described by Bunsen*, the author uses Doyère's trough and Salet's pipette, the last so modified as to admit of the explosion of gases in it. Instead of determining as steam, the volume of water formed in the combustion of hydrocarbons and gaseous mixtures, the author proposes to determine by absorption the amount of oxygen remaining after the explosion and absorption of carbonic anhydride; the oxygen added must in this case be absolutely pure.

B. B.

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* It is to be regretted that Bunsen has not yet described his simple apparatus for transferring gases after the absorption of carbonic anhydride by a solution of caustic soda. This, with many other undescribed pieces of apparatus, has been in use in his laboratory since 1878.—B. B.

Quantitative Estimations by Measurement of Electric Conductivity. By E. REICHERT (*Zeit. anal. Chem.*, **28**, 1—25).—The electric conductivity of a solution is a function of its strength, so that when only a single electrolyte is present, its amount can be ascertained from the conductivity of the solution. The author proposes to call this the *rheometric* method. It can be used with especial advantage for solutions which are too dilute for the densimetric method.

The apparatus consists of a galvanic element, a simple induction coil with alternate currents, packed up so as to be inaudible, a bridge with appropriate means of introducing resistance, a telephone, and the cells for the solutions. These are in the form of pyknometer bottles, with delicate thermometers ground into the necks, and are somewhat varied in construction according to the degree of conductivity to be measured. The conductivity of electrolytes is largely influenced by temperature, the cells are therefore so arranged that contact can be instantaneously made by pushing them into a spring clip at the right moment. The electrodes consist of thin platinum foil fused into the walls of the bottles. To avoid polarisation they are platinised. It is necessary that the cells should stand on a perfectly level surface, otherwise the resistance will be different when measured in opposite directions. The mercury resistance values of the cells is ascertained by filling one of them with a solution of known conductivity—such as a 23·7 per cent. solution of zinc sulphate absolutely free from acid, which according to Kohlrausch has a conductivity of 4·52 Siemens' units (taking mercury as 10^6). The other cells can be compared with the first, using solutions of appropriate conductivity.

The author has employed this method for the determination of the amount of mineral matter in sugar, molasses, &c. The sugar and accompanying organic matters are practically non-conductors. The conductivity is proportional to the amount of ash, and the results for widely varying percentages of ash agree closely with those obtained by chemical methods. Dilute solutions (13 or 26 grams per litre) give the best results, when a correction is made for the conductivity of distilled water. The resistance does not increase with dilution in the same ratio as in pure salt solutions, in consequence of the simultaneous diminution in viscosity. Denoting as the viscosity (z) of a solution the value $\frac{p}{k} = \frac{\text{ash in 100 c.c.}}{\text{conductivity}}$, and plotting the values of p as abscissæ and z as ordinates on a system of rectangular co-ordinates, the curve obtained is in all cases sensibly a straight line. Denoting by b the intercept on the axis of ordinates, and by a the increase of z for 1 per cent. of ash in the usual equation $z = ap + b$, the value of b is almost exactly the same, viz., 0·845, for all the specimens of sugar, molasses, &c., examined, whilst the value of a diminishes with the increase in the percentage of ash in the solid sugar, being roughly proportional to the percentage of sugar divided by the percentage of ash.

The method appears also to have some value for the examination of natural waters. The specific conductivity multiplied by 72·28 gives approximately the number of milligrams of solid residue per litre. It is pointed out that variations in the purity of a water stream could be observed at a distant station by means of the telephone.

M. J. S.

Use of Hydrogen Peroxide in Analysis. By F. P. DUNNINGTON (*Chem. News*, **59**, 76).—The presence of hydrogen peroxide assists the solution of lead peroxide in nitric acid. Precipitated or ignited manganic oxide or ignited ceric oxide also dissolves readily in dilute acids if mixed with hydrogen peroxide. D. A. L.

Estimation of Water in Silicates, such as Tourmalin, Vesuvian, &c. By P. JANNASCH (*Ber.*, **22**, 221—223).—To estimate the water in tourmalin and other minerals, the finely divided substance is dried over calcium chloride for an hour and intimately mixed with a large quantity of very finely divided, dry lead chromate. The mixture is placed in the hinder part of an ordinary bayonet-shaped combustion tube, 46—47 cm. in length, between two layers of finely powdered, dry lead chromate. A rather longer layer of coarsely powdered, dry lead chromate is then placed on each side and lastly a copper spiral. A weighed calcium chloride tube and a weighed soda-lime tube, guarded by a small soda-lime tube, are attached, and the process is then carried out just as in an ordinary elementary analysis. A stream of dry air is passed through the apparatus during the whole operation, and the mixture of mineral and lead chromate should be heated as strongly as possible for about half an hour. The quantity of carbonic anhydride can be estimated at the same time from the increase in weight of the soda-lime tube.

F. S. K.

Source of Error in the Determination of Nitrogen in Substances containing Halogens. By R. ZSIGMONDY (*Zeit. anal. Chem.*, **28**, 58—60).—In determining nitrogen by Dumas' method, and employing cupric oxide containing chloride, the results are apt to come out too high. This is due to the absorption of oxygen by the cuprous chloride (which takes place at 100—300°), when, for the purpose of oxidising the copper reduced in a previous analysis, the contents of the combustion tube are ignited and cooled in a current of that gas. This oxygen is given up again on strong ignition, and may in part be carried over with the nitrogen. It may be arrested by sufficiently increasing the length of the plug of metallic copper in the front part of the tube, but sharper results are obtained by substituting a stream of carbonic anhydride for the oxygen during the cooling after oxidation. With this modification, the use of cupric oxide for the combustion of substances containing halogens is perfectly admissible, and yields highly satisfactory results.

M. J. S.

Estimation of Nitrogen by Kjeldahl's Method. By C. VIOLLETTE (*Compt. rend.*, **108**, 181—183).—The nitrogen in a sample of cake prepared from the residues from the fermentation of maize was estimated by soda-lime, by Dumas' method, and by Kjeldahl's method; these gave respectively the following results: 4·17, 4·29, 4·29 per cent.

Nordhausen sulphuric acid was used instead of the ordinary concentrated acid. Like L'Hote (this vol., p. 438), the author finds that the use of mercury accelerates the operation, but also that in some cases it tends to give low results, probably owing to the formation of some mercury ammonia-derivative which is not decomposed by boiling with sodium sulphide and hydroxide. C. H. B.

Estimation of Nitrogen in Nitrates by Kjeldahl's Method. By O. FOERSTER (*Chem. Zeit.*, **12**, 1555).—0·5 gram of potassium nitrate is dissolved in 15 c.c. of phenolsulphonic acid (5 per cent. phenol), and mixed with 1 to 2 grams of crystalline sodium thiosulphate, being kept cool during both operations; the estimation is then continued in the usual manner. The author's results are 0·09—0·18 per cent. too low, this is attributed to small quantities of ammonia escaping absorption by the acid. (Compare Scovell, this vol., p. 308.) D. A. L.

Detection of Nitrates in Soils. By KREUSLER (*Bied. Centr.*, 1889, 74—75).—The diphenylamine reaction which is employed for the detection of nitrates in soils is not infallible, as salts of ferric and manganese oxide also produce a blue coloration. The brucine reaction is likewise produced by the higher oxides of manganese, although not by iron compounds. E. W. P.

Estimation of Nitrogen and Phosphoric Acid in Organic Substances. By O. LANGE (*Chem. Zeit.*, **12**, 1587—1588).—The following plan allows the estimation of phosphoric acid by the citrate method, and of nitrogen by Kjeldahl's method to be made in the same portion of substance, and gives results which compare well with those obtained in the usual way.

10 grams of the substance is heated with 50 c.c. of concentrated sulphuric acid and 0·5 to 1 gram of copper sulphate in a half-litre flask; when the reaction is complete, the flask is filled to the mark, 50 c.c. of the solution is mixed with 100 c.c. of Märcker's citrate solution and 25 c.c. of magnesia mixture for the estimation of phosphoric acid; whilst the nitrogen is determined in another 50 c.c. by distillation with soda. D. A. L.

Estimation of Phosphoric Acid in Sweet Wines. By W. FRESENIUS (*Zeit. anal. Chem.*, **28**, 67—71).—In wines containing much sugar, a loss of phosphoric acid takes place during the incineration of the residue. A higher result is obtained when the residue is deflagrated with alkaline carbonate and nitrate. Destruction of the sugar by fermentation before incinerating leads to the same result. When time allows, this should be effected by adding only a trace of yeast, since then no correction for the phosphoric acid in the yeast is required, and the amount of organic matter to be burnt is kept as low as possible.

Attention is called to the possibility of manufacturing sweet wines without either the addition of sugar or concentration of the must, by arresting the fermentation at an early stage by the addition of alcohol.

The determination of the glycerol affords the best indication whether this has been the case or not, since with normal fermentation the glycerol should be from 7 to 10 per cent. of the alcohol present.

M. J. S.

Estimation of Phosphoric Acid in the Presence of Ammonium Citrate. By F. SEYFERT (*Chem. Zeit.*, **12**, 1390).—The complete precipitation of ammonium magnesium phosphate (compare Stutzer, this vol., p. 186) or barium sulphate, or calcium oxalate, may be considerably accelerated by stirring 20—30 times with a feather with the barbs cut short, at the same time rubbing it vigorously against the sides of the beaker; as soon as the precipitate has settled to some extent, it may be filtered without pressure, and the whole analysis finished in a fraction of the time usually required.

D. A. L.

The Molybdate Test for Hypophosphites. By E. J. MILLARD (*Pharm. J. Trans.* [3], **19**, 585).—Although it has been stated by Winkler (*Ann. Phys. Chem.* **111**, 443) and others that hypophosphorous acid and hypophosphites give a blue colour or precipitate with ammonium molybdate, the author has never been able to obtain such a reaction with acid, neutral, or alkaline solutions of the molybdate, or he has obtained at most only a faint coloration after a considerable time. On the other hand, he finds that the addition of a small quantity of sulphurous acid renders the test a most delicate one, and one with which the ordinary nitric acid solution of ammonium molybdate answers well. Phosphates, pyrophosphates, and phosphites do not give the reaction when similarly treated. In pure solutions it is possible to detect 1 part of hypophosphorous acid in 2000.

R. R.

Arsenic in Bone Phosphate used for Cattle Feeding. By H. FRESENIUS (*Zeit. anal. Chem.*, **28**, 64—57).—It has long been the practice to mix with cattle fodder a certain quantity of precipitated calcium phosphate, manufactured by treating bones or bone-ash with hydrochloric acid and precipitating with milk of lime. If the hydrochloric acid used contains arsenic this passes into the precipitate, and, according to its proportion, may act either beneficially as a tonic, or injuriously as a poison. To determine it, the method of R. Fresenius and Hintz was found the most advantageous. 10 grams of substance is mixed in a retort with 100 c.c. of hydrochloric acid (1·19) and 5 c.c. of a saturated solution of ferrous chloride, and the acid is distilled off down to a small residue. The whole of the arsenic is obtained in the distillate, which is free from all but traces of organic matter, so that it is in a very suitable condition for precipitation as trisulphide. In 25 samples examined during the past year, the arsenic varied from 0·028 to 0·17 per cent. No data exist for fixing the admissible maximum in a cattle food.

M. J. S.

Apparatus for the Electrolytic Estimation of Metals. By L. C. LEVOIR (*Zeit. anal. Chem.*, **28**, 63).—The solution to be electrolysed is contained in a large platinum basin resting upon three metallic knobs connected with the positive pole of the battery. The cathode consists of a smaller platinum basin suspended concentrically within the former at a distance of about 30 mm., by means of three wires and a hook which dips into a pool of mercury in the wooden arm of the stand. The evolution of oxygen which takes place at the surface of the larger basin keeps the liquid well mixed and facilitates the rapid and regular deposition of the metal on the outside of the inner basin. M. J. S.

Estimation of Zinc in presence of Manganese. By G. NEUMANN (*Zeit. anal. Chem.*, **28**, 57—58).—The author had studied the precipitation of zinc from a formic acid solution before the publication of the method by Bragard (Abstr., 1888, 689). The process affords a simple, rapid, and accurate separation of zinc from manganese, iron, and nickel. M. J. S.

Volumetric Estimation of Lead in presence of Tin. By YVON (*J. Pharm.* [5], **19**, 18—21).—Having had occasion to make a number of determinations of lead in presence of tin, the author devised a method which requires neither the separation of the tin nor the washing of precipitates. The lead-tin alloy is treated with nitric acid, by which the lead is dissolved and the tin converted into insoluble stannic acid. The excess of nitric acid is neutralised by the addition of a very slight excess of sodium hydroxide, and a few drops of acetic acid in excess are added. The solution is then diluted so as to contain not less than ½ per cent. of lead, and titrated with normal potassium ferrocyanide solution (10·201 grams per litre) which has been standardised against a normal lead nitrate solution (15·987 grams per litre), using drops of dilute ferric chloride solution on a porcelain slab as indicator. The process is very rapid and sufficiently exact for many purposes. J. T.

Testing Glass by Colour Reactions. By F. MYLIUS (*Ber.*, **22**, 310—314).—An aqueous solution of iodine kept in sealed tubes for a few weeks is completely decolorised owing to the action of the alkalis contained in the glass; on adding dilute sulphuric acid, the solution again becomes coloured. When a trace of a very dilute solution of silver acetate or nitrate is added to an aqueous solution of starch and pure iodine the latter becomes yellowish or colourless, owing to the combination of the free hydriodic acid; if, now, a little powdered glass is added the solution is at once coloured blue owing to the formation of an alkaline iodide. (Compare Abstr., 1887, 568.) Experiments showed that the depth of colour produced in such solutions in a quarter of an hour by lead crystal glass, Thüringer glass, thermometer glass from Zena, and Bohemian glass, was greatest in the case of the lead glass and gradually decreased in the order given.

The following method can be employed for testing the quality of glass:—The surface to be tested is first carefully washed with water, alcohol, and ether consecutively, and then covered with, or in the case of tubes filled with, a solution of iodoeosine (0·1 gram) in ether (100 c.c.) which has been previously saturated with water at the ordinary temperature; after keeping for 24 hours, the glass is washed with ether. The surface will then be covered with a red layer, purple in transmitted light, the intensity of the colour varying with the degree to which the surface has been attacked. The coloured layer is generally homogeneous and transparent, but in very bad samples it is dull and crystalline; bad glass, moreover, cannot be freed from alkali by washing with water, so that the red colour is formed immediately, whilst with samples of good glass the colour is only produced after several hours.

The principle of the method is that the free alkali produced by the action of the water in the ether, and the slight additional action of the "eosine acid," combines with the iodoeosine, forming a salt which, being insoluble in ether, is deposited on the glass.

Experiments show that this method leads to the same conclusions as Weber's hydrochloric acid method (*Dingl. polyt. J.*, **171**, 129). Glass containing lead is strongly attacked, and the mixture of lead and alkaline salts deposited on the surface can be separated by washing with water, the former remaining undissolved. Very slight variations in the surface can be detected; the difference in the intensity of the coloured layers produced with samples of the same glass, one of which has been kept in contact with cold water or dilute acids for 24 hours, or heated with water for five minutes, is distinctly noticeable.

If a glass tube, which has been submitted to electrolysis by Warburg's method, is tested, it is seen that the surface which was in connection with the anode does not become coated as it is free from alkali, the other surface, however, becomes covered with a deep-red layer, showing that the proportion of alkali has been increased by electrolysis.

The worst glass can be made capable of permanently resisting the action of water by first leaving it in contact with cold water for several days and then heating to 300—400°. After this treatment, no coloration is produced with the iodoeosine solution even after several months' time, whereas the original material and some which had been heated only to 100° give a deep-red coloration in a few hours. When the better kinds of glass are treated with water, the difference caused by the subsequent heating is not so marked.

In testing glass tubes, a colourless zone is frequently observed a little above the sealed end. This phenomenon is due to the primary formation of a layer of moist silica which, on heating at 300—400°, becomes impervious to water; at the end of the tube this layer merges into the melted glass which again becomes hygroscopic on solidifying. The inverse phenomenon occurs when tubes are sealed without having been previously cleaned. The alkaline compounds fuse on the surface of the glass, and even after washing with water, alcohol, and ether, the iodoeosine test shows a region rich in alkali; at the end of the tube, however, the alkalis have dissolved in the melted glass.

Freshly broken surfaces even of the best glass, immediately become covered with a thin red layer when thus tested. F. S. K.

Separation of Aluminium and Zirconium. By I. T. Davis, Junr. (*Amer. Chem. J.*, **11**, 26—29). — Quantitative experiments proved that zirconium is almost completely precipitated from neutral or feebly acid solutions by sodium iodate, the error amounting to

1 per cent. of the zirconium employed. The precipitate is probably an oxyiodate; when heated, it is readily and completely converted into the dioxide. As aluminium iodate is readily soluble in water, the author has experimented with the following method, which gives, as the analyses show, very good results. The hydrochloric acid solution of the two metals is neutralised with an excess of sodium carbonate until a permanent precipitate is formed. The precipitate is redissolved in the smallest quantity of hydrochloric acid, and sodium iodate added in excess. The solution is heated for about 15 minutes, allowed to remain about 12 hours, filtered, the precipitate washed with boiling water, dissolved in hydrochloric acid, precipitated with ammonia, ignited, and weighed. All iron salts must be previously separated. A convenient amount of zirconium to work with is 0·1 gram ZrO_2 in 100 c.c. J. W. L.

Direct Estimation of Oxygen and Nitrogen in Natural Waters. By A. Lalieu (*J. Pharm.* [5], **19**, 147—150).—The mixed gases are boiled off, collected in a eudiometer and measured; the oxygen is then absorbed by means of an alkaline pyrogallol solution. and the residual gas is measured again. A very small, wide-necked flask of 8 to 10 c.c. capacity has an internal diameter of 18 to 20 mm., to this is fitted a perforated stopper carrying a small cylindrical funnel with a narrow tube about 4 cm. long, stiffly held by the stopper. Supposing the gases to be in the eudiometer, and this being plunged in the water of the pneumatic trough, the small flask is charged with 4 c.c. of normal alkali solution; then 0·10 gram of pyrogallol is added, and the flask is filled completely with water, the stopper is inserted so that the liquid is forced into the head of the funnel tube: this is covered with the finger, and the liquid is agitated. The flask is now plunged into the water of the trough, the funnel filled with water, and the flask turned upwards so that the gas can be easily transferred from the eudiometer to the flask. The gas at first stays in the funnel, but by gently drawing out the stopper it can be passed bubble by bubble into the flask. After about an hour the oxygen is completely absorbed, and the residual gas can be directly transferred to the burette, after withdrawing the funnel and stopper. J. T.

Loss on Ignition in Water Analysis. By T. M. Drown (*Chem. News*, 59, 82—83).—The following plan for the estimation of organic matter in waters, by the ignition of the total solid residue left after evaporation, gives lower, and more constant and trustworthy results than the method of direct ignition generally employed. The platinum dish containing the residue is supported on a platinum wire coil or triangle in a larger platinum dish, which is kept at a moderate red heat and serves as a radiator; a platinum plate suspended about an inch above the inner dish expedites the ignition. When examining subsoil waters, they are first treated with a measured quantity of sodium carbonate, by which means the inconvenience of hygroscopic residues and the volatilisation of the chlorine or nitric acid are avoided, and the loss on ignition, after due allowance has been made for the sodium carbonate added, represents approximately the organic matter. D. A. L.

Detection of Nitrobenzene in Presence of Oil of Bitter Almonds. By K. LIST (*Chem. Zeit.*, **12**, 1727).—The substance is warmed with soda and a few drops of ferrous sulphate to remove any hydrocyanic acid; plenty of permanganate is then added to destroy the oil of bitter almonds, after which any nitrobenzene present can be recognised by its odour. D. A. L.

Examination of Commercial Alcohol. By H. BORNTRÄGER (*Zeit. anal. Chem.*, **28**, 60—62).—The chief impurities to be sought for are aldehyde, acetal, and amyl alcohol. A sample is mixed with much water. If oily drops separate on the surface, these are tested by adding an equal volume of strong sulphuric acid and then strong potash, when acetal gives an odour of acraldehyde, whilst amyl alcohol yields an agreeable odour; further, by adding 3 drops of concentrated hydrochloric acid and 10 of colourless aniline, amyl alcohol then gives a rich raspberry-red coloration, whilst acetal produces no colour. Aldehyde gives a deep-brown colour with a strong solution of potassium iodide. With a colourless mixture of rosaniline and sodium hydrogen sulphite, it yields a strong violet colour, becoming blue on addition of concentrated hydrochloric acid. Acetal and amyl alcohol give no colour with either of these reagents. A specimen of the alcohol is mixed with 2 parts of water and shaken with chloroform, which is then separated and allowed to evaporate at a moderate temperature. The residue is tested for acetal and amyl alcohol as above. A spirit which gives no coloration with an equal volume of concentrated sulphuric acid or of strong potash (1 : 3) is practically free from the above impurities. M. J. S.

Detection of Sugar in Urine. By L. CRISMER (*Arch. Pharm.* [3], **26**, 1134, from *Ann. soc. méd. chir. de Liège*, October, 1888).—1 c.c. of urine is heated to boiling with 5 c.c. of a 0·1 per cent. aqueous solution of safranine and 2 c.c. of a 10 per cent. sodium hydroxide solution. If it is decolorised, sugar is present, as even 0·001 gram of glucose in 1 c.c. of urine is sufficient to produce this effect. It may happen that a urine failing to react with Fehling's solution decolorises safranine solution, but the converse never happens. The foreign Abstractor remarks that Fehling's solution sometimes reacts when no sugar is present, in which cases safranine would have the same fault; but where Fehling's solution is not reduced, although sugar is present, then probably the safranine test would have the advantage (compare, however, Crismer, this vol., p. 446). J. T.

Estimation of Sorbite. By C. VINCENT and DELACHANAL (*Compt. rend.*, **108**, 147—148).—See p. 478.

General and Physical Chemistry.

Absorption-spectra of Epidote. By H. BECQUEREL (*Compt. rend.*, **108**, 282—284; compare *Ann. Chim. Phys.* [6], **14**, 170).—When the luminous vibrations traverse a crystal of green epidote in a direction parallel with the axis of symmetry, almost all the visible spectrum is absorbed, but if the direction of the vibrations is parallel with the plane of symmetry *g*, several absorption-bands are visible, and these disappear one by one as the orientation of the crystal is varied. The bands observed are a somewhat weak band, γ, in the orange, which has a mean wave-length of 603, and extends to D; a group, β, composed of three broad and intense bands with the same principal directions and mean wave-lengths of 473·5, 456·7, and 429 to 425; a narrow and very intense band, α, with a mean wave-length of 453·4, which is only visible when the absorption of the group β is at a minimum. When the absorption of the group β is at its maximum, the three bands coalesce, and the absorption extends through the whole of the green region up to G. Measurements of the azimuths of these bands with respect to the two optical axes, are given in a table. The anomalous principal directions of the bands α, β, γ show that they are due to three different substances, and their relative intensities vary considerably in different samples of epidote. It is not yet possible to attribute the bands to any particular elements, but γ is similar to a band seen in cobalt glass, β may be due to iron, and α resembles a band which is visible in the ordinary, but not in the extraordinary spectrum of idocrase. C. H. B.

Change of Fluorescence with Concentration. By B. WALTER (*Ann. Phys. Chem.* [2], **36**, 502—518).—In a recent paper (Abstr., 1888, 881), the author describes some investigations from which he had come to the conclusion that the fluorescence of a liquid increases without limit as the dilution increases. He has since found that Lommel (*Ann. Phys. Chem.*, **160**, 70) had come to the same conclusion. The author has recently carried out a further series of researches on the ammonium salt of fluoresceïn, obtained by saturating a concentrated aqueous solution of ammonia with fluoresceïn. By the aid of the mathematical investigation given by Lommel in the paper referred to, the author has succeeded in elucidating the phenomena more completely, and he finds that the law first stated by Lommel, and obtained independently by himself, required some modification. The result of the present investigation is that the fluorescence of a concentrated solution of the salt is zero, or, at any rate, too small to be observed. When water was gradually added, the fluorescence first attained a measurable value for a concentration of 1/25, and rapidly increased with further dilution until the concentration was reduced to 1/3200, after which it remained constant as far as the observations extended, namely, to a concentration of 1/6553600. Similar results were obtained with an alcoholic solution of Magdala-red, except that it was impossible to obtain very concentrated solutions of this substance, so that it was impossible to observe the beginning of the fluorescence.

G. W. T.

Evidence afforded by Fluorescence and Absorption of the Decomposition of Molecular Groups in Solutions. By B. Walter (*Ann. Phys. Chem.* [2], **36**, 518—532).—The fact that fluorescent liquids lose the power of fluorescence when they become sufficiently concentrated, suggested to the author that possibly the groups of molecules existing in the solid salt were only partially dissociated in the concentrated solution, but became more and more so with increasing dilution, until when the fluorescence was no longer affected by further dilution, the dissociation was complete. Assuming this to be the case, the author calls a solution "complete" when the dissociation is perfect, and "partial" when it is imperfect.

Now, according to Beer's law of absorption, a given quantity of substance in solution will absorb the same quantity of light whatever be the strength of the solution, but in the case of fluoresceïn he finds that this only holds good when the dilution has gone beyond the critical point for which the fluorescence ceases to increase with further dilution, and for the more concentrated solutions, the absorption depends on the concentration: for example, in the case of solutions of concentration 1/800, 1/400, 1/200, 1/100 respectively, the coefficients of transmission for light corresponding with the line D in the spectrum, were for a thickness of 1 mm. of the solution, 0·965, 0·878, 0·602, and 0·230, whilst according to Beer's law they should be 0·965, 0·931, 0·867, and 0·752; the deviations therefore increase with the distance from the critical point. Similar results were obtained in the case of partial and complete solutions of several other substances, some fluorescent and some not. Beer's law, therefore, requires correction, and may be re-stated as follows: The absorptive or fluorescent power of a single molecule in a solution remains constant so long as the molecule is not joined into a group with others. The author observed in the course of his previous investigations (Abstr., 1888, 883), but without understanding the reason, that when a vessel containing a fluorescent substance is illuminated by light from a bright line spectrum, if the concentration of the liquid is gradually increased, the fluorescent light which at first corresponds exactly with the absorption ceases to do so after a certain concentration has been reached, and whilst the fluorescence extends only up to a certain portion of the spectrum, starting from the ultra-violet end, the absorption extends ultimately over the whole of the spectrum when the concentration becomes sufficiently great. Experiments of this kind made with fluoresceïn, Magdala-red, and æsculin, show definitely that the solutions in which the fluorescent light corresponded with the absorption, were all complete solutions, and that the concentration at which fluorescence ceased to correspond with the absorption, was the critical one at which the solution passed from a complete to a partial one. The results of these observations led the author to the following conclusions:—(1.) In the partial solutions of the substances experimented on, single molecules and molecular groups exist together, and as concentration increases the number of the latter increases at the expense of the former. (2.) Only single molecules have the power of fluorescing. (3.) The single molecule has its known definite sphere of absorption in the spectrum, whilst the absorption of the molecular groups extends also to the neighbouring portions of the spectrum. There are, therefore, three reasons in virtue of which the fluorescence of a partial solution should diminish with increasing concentration; (1), because the number of single molecules is diminished; (2), because the molecular groups which are formed absorb ever-increasing portions of the incident light; (3), because these groups also absorb an increasing portion of the fluorescent light emitted by the single molecules. The third law, therefore, as stated by the author, affords a means of determining by optical means whether a non-fluorescent colouring matter does or does not exist in solution in more than one state of molecular aggregation, and if it can exist in more than one state, an estimate of the degree of aggregation may be formed by measuring the breadth of the partial shadow existing on each side of the dark lines of the absorption-spectrum produced on passing white light through a moderate thickness, say 50 mm. or upwards, of the solution. The author gives several examples of actual measurements made in this way in the case of solutions of the fluorescent substances, fluoresceïn and Magdala-red, and also the non-fluorescent substances, iron chloride and copper chloride. In the case of the last two there was evidence from other sources of their existing in solution in different states of molecular aggregation. In all these cases it was found that the breadth of the absorption-bands increased largely with the concentration of the solution. Another interesting observation made by the author was, that solutions of fluoresceïn and eosin in water had their fluorescent power increased by heat, the effect of which would be to increase their solubility, whilst, on the other hand, an alcoholic solution of Magdala-red, which is less soluble in hot water than in cold, had its fluorescent power diminished by being heated. This also explains the well-known fact that an aqueous solution of Magdala-red, which is more soluble in hot water than in cold, acquires fluorescent properties when it is heated, although it does not possess them when cold. G. W. T.

Electromotive Force of Selenium. By A. Righi (*Ann. Phys. Chem.* [2], **36**, 464—465).—This is a reply to some strictures made by Kalischer (this vol., p. 3) on some previous investigations of the author, according to which a current can be obtained from a selenium cell in the dark as well as under the influence of light; although the effect of light is to increase the current, not only by diminishing the resistance of the selenium but by increasing the E.M.F. of the cell. He had also found that the effect of pressure on the selenium was to diminish the E.M.F. of the cell. Kalischer maintained that these results were really residual effects, due to the previous exposure of the cell to the action of light. The author has now repeated his experiments with cells which were prepared in the dark and connected by means of insulated wires passing through one of the walls of the room, with testing instruments in another room, so that the cells were not exposed for a single moment to the action of light after the selenium had been obtained in the sensitive condition. The author finds that these cells give exactly the same results as those which had been exposed to light during and subsequent to the process of manufacture. G. W. T.

Production of the Current in the Galvanic Circuit. By L. SOHNCKE (*Zeit. physikal. Chem.*, 3, 1—10).—The author makes use of the contact and dissociation hypotheses, together with the fundamental idea that the attraction of substances for one another is by no means capable of explaining the formation of the current in the galvanic circuit. The method of reasoning is instanced in the case of the polarisation current of an ordinary water voltameter. The positively charged hydrogen attracts the negatively charged free ions, O and SO_4, present in the solution, which therefore combine with the hydrogen, giving up their charges at the one platinum plate, while at the other the negative oxygen attracts the positive hydrogen, which combines with it and gives up its charge. As the source of the energy of the current, the author regards the force originally required to separate the active substance into its ions. H. C.

Electrical Conductivity and Electrolysis of Concentrated Solutions of Sulphuric Acid. By E. BOUTY (*Compt. rend.*, **108**, 393—395).—Kohlrausch showed that sulphuric acid of the composition H_2SO_4 and H_2SO_4,H_2O have lower conductivities than any other mixtures or compounds of the acid with water. The author has determined the conductivity of acid varying from sp. gr. 1·833 to 1·032, and of acid containing 221, 555, and 1110 mols. of water respectively for each molecule of sulphuric anhydride. The specific conductivity shows a first maximum when the composition of the acid is $2H_2SO_4 + H_2O$, a minimum when the composition is $H_2SO_4 + H_2O$, and a second maximum at $H_2SO_4 + 15H_2O$. These maxima and minima are not displaced when the temperature varies from 0° to 18°. The molecular conductivity is at a minimum with the composition H_2SO_4,H_2O, and increases continually for all degrees of greater dilution, the limit being reached when one molecule of dissolved H_2SO_4 has a conductivity 200 times greater than that of the same molecule in the form of the hydrate H_2SO_4,H_2O. The only crystallisable hydrate, H_2SO_4,H_2O, is characterised by its physical properties even when in the liquid state. Its refractive index is the maximum for all rays, its absolute and molecular conductivity is the minimum at all temperatures, and it seems that this is true also of its mobility (*Ann. Phys. Chem.*, **151**, 378). No hydrate containing more water has yet been isolated, but Mendeleeff's results point to the existence of a hydrate, $H_2SO_4 + 5H_2O$ or $+ 6H_2O$, and a second, $H_2SO_4 + 15H_2O$.

The electromotive force of polarisation of platinum electrodes is 1·2 to 1·3 volts with the strongest acid, but gradually diminishes with dilution until it is only 0·7 to 0·8 volt when the composition is H_2SO_4,H_2O. It retains this value until the composition of the liquid becomes $H_2SO_4 + 5H_2O$ or $6H_2O$, and at this point it rises suddenly to 1·4 volts, but afterwards gradually although very slowly diminishes.

A molecule of the type H_2SO_4,H_2O should split up into hydrogen, sulphuric anhydride, and hydrogen peroxide. As a matter of fact hydrogen peroxide is a normal product of the electrolysis of acid of this strength. According to Richarz (*Ann. Phys. Chem.*, [2], **24**, 183), the maximum amount of hydrogen peroxide is obtained when the acid has the composition $H_2SO_4 + 1{\cdot}347H_2O$. With acid below 60 per cent., very little hydrogen peroxide is formed, but persulphuric acid and ozone are produced in considerable quantities. It may be assumed that the apparent limit at $H_2SO_4 + 5H_2O$ or $6H_2O$ really corresponds with the complete disappearance of hydrogen peroxide from the products of electrolysis, or in other words, with the complete destruction of molecules of the type H_2SO_4,H_2O, whilst the limit at $H_2SO_4 + 15H_2O$ corresponds with the complete disappearance of persulphuric acid from the products, or with the destruction of the unknown hydrate intermediate between the monohydrate and that which exists in very dilute solutions. C. H. B.

Electrical Conductivity of Solid Mercury. By C. L. WEBER (*Ann. Phys. Chem.* [2], **36**, 587—591).—This is a reply to L. Grunmach (this vol., p. 201), who criticised the results obtained by the author in a former investigation (Abstr., 1885, 1028), and by Cailletet and Bouty (Abstr., 1885, 855). The author states that his observations had been made with comparatively simple apparatus, and he considers it probable that there may be slight deviations from accuracy, but he does not admit that the corrections required can be anything like sufficient to account for the difference between his results and those of Grunmach. He further points out that his results and those of the two French physicists mentioned are in close accordance, and he traverses in detail some of Grunmach's objections to his methods of experimenting. G. W. T.

Electrochemical Measurement of Currents. By A. POTIER (*Compt. rend.*, **108**, 396—398).—When solutions of silver nitrate and mercurous nitrate contained in similar voltameters are enclosed in the same circuit, the quantities of metal deposited are not in the exact ratio of their atomic weights, and the difference may amount to 2 per cent. If mercurous nitrate is electrolysed with platinum electrodes, there is at first an evolution of hydrogen at the cathode, and this does not cease until the whole surface of the cathode is covered with mercury. A second cathode immersed in the liquid shows the same phenomenon, and it is therefore not due to the presence, at the commencement, of a small quantity of free acid which is destroyed as electrolysis proceeds. Cathodes of silver and copper give similar results, but it is somewhat longer before the evolution of gas ceases. With a cathode of metallic mercury, no hydrogen is evolved, but the metal is strongly polarised. It would seem that in all cases hydrogen is liberated at the cathode and is occluded, but is removed by diffusion or some other cause.

From these results it follows that the use of a cathode consisting of the metal which is to be deposited does not in every case prevent polarisation. C. H. B.

Free Ions. By W. OSTWALD and W. NERNST (*Zeit. physikal. Chem.*, 3, 120—130).—The authors advance further theoretical and experimental evidence in favour of the view that electrolytes contain free ions. Among others the following experiment is described:—A glass tube provided with a tap is drawn out at one end to a capillary, and filled with mercury. The capillary is then immersed in dilute sulphuric acid, and the apparatus so adjusted that the acid fills one half of the capillary. By means of a damp thread, the acid solution is then connected with a similar solution contained in a flask, the outside of which is coated with tinfoil; this is placed on an insulated stand. The tinfoil receives a positive charge from an electrical machine, and on then connecting the mercury to earth, bubbles of hydrogen appear at the junction of the mercury with the acid. The explanation given is that the positive charge of the foil attracts the negatively charged ions, whilst the positively charged ions are repelled and accumulate at the mercury. On connecting to earth, the ions give up their charges, and are therefore set free.

Other similar experiments are described, and it is likewise shown that in accordance with thermodynamical principles the ions must be already present in the solution in a free state, and that no part of the charge is used up in their liberation. H. C.

Electrolysis. By VIOLLE and CHASSAGNY (*Compt. rend.*, **108**, 284—287).—If a positive electrode consisting of a platinum wire 4·5 mm. in diameter is plunged to a considerable depth in water containing 10 per cent. of sulphuric acid, and a negative electrode consisting of a platinum wire 1·5 mm. in diameter is gradually immersed in the liquid, then, if the difference of potential between the two electrodes is not less that 32 volts, there is seen round the negative electrode a luminous sheath which separates it from the liquid and in which alone the evolution of hydrogen takes place. This sheath offers a very high resistance, which gradually diminishes as the length of wire immersed increases, and falls very suddenly at the moment when the luminous sheath disappears and gives place to a train of bubbles of hydrogen. The length of the luminous sheath increases with the electromotive force, and the quantity of energy used up in the electrolytic cell is proportional to the length of the luminous sheath which the particular current can produce. The luminosity is not continuous, and at first it consists only of points of orange light at the extremity of the electrode, but these become violet in colour and extend over the whole of the submerged wire. The electrodes become very hot, and if the circuit is broken the luminosity does not disappear immediately, and there is a hissing sound when the water comes in contact with the hot wire. The displacement of the luminous sheath by a train of bubbles of gas, which takes place when the electrode is immersed to a certain depth, is accompanied by a kind of explosion. The connection between the luminous effect and temperature is shown by the fact that even with a difference of potential somewhat below 32 volts, which is not sufficient to produce the sheath, it appears for a short time if the electrode is heated. With a sheath of any given length, an increased difference of potential produces increased intensity of the calorific and luminous effects, the sheath enlarges, evolution of gas is accelerated, and large bubbles of gas escape with a hissing noise. With a sufficiently high electromotive force, the electrodes may become red hot and may even fuse. Under such conditions it becomes very difficult to produce and maintain the luminous effect, since the sheath so readily gives place to a rapid train of bubbles of gas, which rise to the surface with a series of small explosions. This audible electrolysis is accompanied by disintegration of the electrodes, and a heavy black powder separates, which has the composition Pt_2H and decomposes in a vacuum above 400°.

Similar effects are observed when the smaller wire is made the positive electrode. A difference of potential of not less than 50 volts is required, but on the other hand the effects are more persistent. The luminous sheath may indeed be made to appear at either of the electrodes according to their relative temperatures. C. H. B.

Electrolysis of Solutions of Hydrogen Fluoride and of Potassium Antimonate with Carbon Electrodes. By A. BARTOLI and G. PAPASOGLI (*Chem. Centr.*, 1889, 177, from *L'Orosi*, **11**, 397—400).—If in the electrolysis of concentrated hydrofluoric acid a carbon positive electrode is employed, it disintegrates and falls to pieces, and yields, after purification, an impalpable powder, which is partly soluble in concentrated sulphuric acid. When treated with sodium hypochlorite, this substance yields considerable quantities of sodium fluoride and mellitic acid. In the case of a solution of potassium antimonate, the carbon pole is also rapidly attacked, and a black substance is precipitated, somewhat soluble in water, and containing antimony. It is soluble in alkalis, and is oxidised by sodium hypochlorite to mellitic and other acids of the benzene series. The authors name this substance *stibiomellogen.* J. W. L.

Conductivity of Mercury Vapour for Heat. By L. SCHLEIERMACHER (*Ann. Phys. Chem.* [2], **36**, 346—357).—In a former investigation (*ibid.* [2], **34**, 623) on the heat conductivity of air, hydrogen, and carbonic anhydride, the author obtained values for the conductivity differing from those calculated from theory. Either of the theories can, however, be brought into agreement with the observations by making certain assumptions as to the distribution of the intramolecular energy in the conduction of heat in diatomic and polyatomic gases. The simplest assumption would be that the intramolecular energy is propagated with the same velocity as the molecular energy. Boltzmann's theory would then, however, lead to values greater than those given by observation, whilst O. E. Meyer's theory would lead to values smaller than those observed. Now it appears extremely improbable that the intramolecular energy can be propagated with a greater velocity than the molecular energy, and therefore the author was inclined to believe that Meyer's theory does not correctly represent the facts. In order to decide definitely between these two theories, it was necessary to determine the conductivity for heat of a monatomic gas, for which the assumptions made would be indifferent. With this object in view, he undertook the investigation of the heat conductivity of mercury vapour described in the present paper. The method adopted for the determination was the same as that which he had previously employed, but owing to the difficulty introduced by the fact that the temperature had to be above 180°, the results obtained are not equally trustworthy. The author finds as the mean value of the conductivity k, at the temperature 203°, the value 0·00001846 C.G.S. water units. The temperature coefficient of the conductivity determined from the means of the observed values at 182·5° and 215° respectively was 0·0074. On account of the various errors of observation incidental to the experiment, this result cannot be regarded as extremely trustworthy, but as far as it goes it does not differ greatly from what would be expected from theory, for in the case of monatomic gases at constant specific heat the conductivity should depend on the temperature in exactly the same way as the coefficient of viscosity. Now, according to Koch (*Ann. Phys. Chem.* [2], **19**, 870) the relation between this coefficient and the temperature is given by the formula $\mu = \mu_0(1 + \alpha t)^{1·6}$, where $\alpha =$ 0·003665 and μ is the coefficient of viscosity. If the relation between the conductivity and the temperature is expressed by means of a similar formula, the value of the exponent is found to be 1·4. According to all existing theories, the conductivity k of a monatomic gas is proportional to the product of the viscosity coefficient η and the specific heat at constant volume c_v, so that $k/\eta c_v$ has the same value for all monatomic gases. There is little doubt that this is correct, and it agrees with the fact of observation that the conductivities of gases and also their coefficients of viscosity are independent of the pressure. The numerical value of this expression, however, is different according to the different theories, being 2·5 according to Boltzmann's hypothesis that the molecules exert a repulsive force on one another varying inversely as the 5th power of the distance, whilst according to O. E. Meyer its value should be 1·53. Taking Koch's value for the viscosity coefficient of mercury vapour, the value is found to be 3·15, which is more than double the value according to Meyer, and about 25 per cent. too great according to Boltzmann. This result shows conclusively that Meyer's theory does not represent the facts. The deviation from Boltzmann's value might possibly be attributed to the comparatively large errors of observation inseparable from the method of experiment. The following consideration, however, led the author to believe that the value 3·15 is rather too small than too great, and that therefore Boltzmann's theory must also be rejected. In order to explain conduction in polyatomic gases, according to the latter theory, it is necessary to make some assumption as to the part played in the conduction by the intramolecular energy. One of the assumptions which may be made is that the internal or progressive energy is distributed in exactly the same manner when heat conduction is going on as when there is a uniform temperature throughout. This assumption (a) leads to the conclusion that the conductivity of any gas is given by an expression of the form $k = C_a \eta c_v$, where C_a is a constant. Another possible assumption (b) is that the transference of heat is entirely due to the progressive energy of the molecules, in which case $k = \frac{5}{2}C_b(K - 1)\eta c_v$, where K is the ratio of the specific heat at constant pressure to that at constant volume and C_b is a constant. If, then, observation shows that for all gases $C_a = K/\eta c_v$ has the same value as in the case of mercury vapour, the assumption (*a*) may be assumed to be correct. If, however, $C_b = K/(\frac{3}{2}(K - 2)\eta c_v)$ is constant for all gases, assumption (*b*) is confirmed. It may be, however, that neither of these represents the state of things, and that the internal energy plays a part in the conductivity but to a lesser extent than is assumed by (*a*). In this case, the value of the first expression will be smaller and that of the second greater than for mercury vapour. Taking the values of η determined by O. E. Meyer (*Wien. Ber.*, **73**, 433) for mercury vapour, air, hydrogen, and carbonic anhydride, and the values of K determined for the same gases by A. Wüllner (*Ann. Phys. Chem.* [2], **4**, 321), the author finds that the values of C_a and C_b are as given below:—

	k.	C_a.	C_b.
Mercury	0·0000185	3·15	3·15
Air	0·0000562	1·98	3 26
Hydrogen..........	0·0004100	1·94	3·35
Carbonic anhydride .	0·0000327	1·59	3·40

This table shows that the hypothesis (*a*) must be rejected. The hypothesis (*b*) appears to agree well with experiment for the three polyatomic gases, and the values obtained for these do not differ from that obtained for mercury by more than 6 per cent. This difference may be due to errors of observation, but it may on the other hand be caused by intramolecular energy in the case of the polyatomic gas playing a part in the conductivity, but to a very much smaller extent than assumed by (*a*). In either case, the conclusion to be drawn is that in the above-mentioned gases the conduction of heat is mainly due to the transference of progressive energy only. The author then calculates the values of C_a and C_b from the results of Winkelmann's observations on carbonic oxide, nitrous oxide, and ethylene, and the results are given below:—

	k.	C_a	C_b.
Carbonic oxide	0·0000499	1·94	3·20
Nitrous oxide	0·0000350	1·84	3·94
Ethylene	0·0000395	1·71	4·66

These numbers show that neither (*a*) nor (*b*) exactly represents the truth, but that this lies, as previously suggested, between the two. The conclusions arrived at in this paper of course depend on the assumption that the conduction of heat in a gas is entirely effected by the motion of its molecules, and that there is no internal radiation from molecule to molecule. If such internal radiation took place to any extent the values of *k* for air, hydrogen, carbonic oxide, and carbonic anhydride could not agree so well together, as the absorptive power of carbonic anhydride is very high compared with that of the other three gases. Internal radiation could not therefore take place to a sufficient extent to explain the deviations from Meyer's theory, but the author considers that it may possibly occur to a certain extent, and as nothing is known about the absorptive power of mercury vapour, he does not feel justified in concluding that the great difference between the values of k for these gases, and that obtained for mercury vapour, conclusively disproves Boltzmann's theory. G. W. T.

Heat of Formation of Aniline Dichromate. By C. GIRARD and L. L'HOTE (*Compt. rend.*, **108**, 238—240).—When a dilute solution of aniline hydrochloride is mixed with an equivalent quantity of aniline or of hydrochloric acid there is no sensible thermal disturbance, and hence it follows that aniline hydrochloride is a stable salt even in dilute solutions. If potassium dichromate is added to an equivalent quantity of aniline hydrochloride solution there is a very slight reduction of temperature, and when this is corrected for the heat absorbed by the dilution of the aniline solution it is found that the reaction absorbs 0·1 Cal. The heats of neutralisation of hydrochloric acid and chromic acid by potassium are 16·7 Cals. and 13·5 Cals. respectively. Direct combination of aniline with chromic acid in the proportion to form aniline dichromate liberates + 7·2 Cals. or + 0·2 Cals. less than the combination with hydrochloric acid. This difference is exactly the same as in the case of the same two acids and potassium. C. H. B.

Alcoholates of Monosodium Glycol. By DE FORCRAND (*Compt. rend.*, **108**, 240—242).—The compounds of monosodium glycol with one molecule of methyl, ethyl, or propyl alcohol are readily obtained by dissolving sodium in three or four equivalents of the particular alcohol and then, after cooling, adding the equivalent of glycol, and evaporating at 120—140° in a current of hydrogen until crystallisation commences in the hot liquid. No glycol is given off in this operation, and hence it has completely expelled the monohydric alcohol from its combination with the sodium. The alcoholates separate in colourless needles or lamellæ, and can be dried on porous plates. The first column gives the heats of dissolution, the second the heats of formation in solution, and the third the heats of formation of the solid alcoholate from the solid glycol-derivative and the liquid alcohol :—

Methyl alcoholate....	+1·97	+0·11	+6·14
Ethyl "	+3·51	−0·03	+5·01
Propyl "	+2·67	−0·03	+6·42

These results were confirmed by measuring the heat developed, on addition of an equivalent quantity of sulphuric acid. The alcohols can be expelled at 130—150° in a current of dry hydrogen, but are not given off over sulphuric acid at 13°. Similar compounds seem to be formed by butyl and amyl alcohols, but they are not readily isolated.

Glycol displaces monhydric alcohols from their metallic derivatives, and the heats of combination of the alcohols with monosodium glycol are higher than their heats of combination with monosodium glyceroxide. Moreover, the heat of combination of monosodium glycol with glycol is higher than its heat of combination with ethyl alcohol.

C. H. B.

Compressibility of Hydrogen. By S. v. WROBLEWSKI (*Monatsh.*, 9, 1067—1125).—The present paper contains the results which had been obtained by the late author up to the time of his death, in his work on the compressibility of hydrogen. It is taken from manuscripts which he had already prepared for publication.

The behaviour of gases at the ordinary temperature on compression is such, according to the experiments of Regnault and Amagat, that the product of pressure into volume, *pv*, at first decreases with rising pressure, until a minimum is reached, and then with every further increase of pressure continually increases. All gases behave in this manner with the exception of hydrogen. Hydrogen shows no decrease and no minimum of *pv* with rising pressure, but the product continually increases with the pressure. This holds for all pressures from one atmosphere upwards, and therefore if the minimum *pv* does occur at all in the case of hydrogen, it must take place at a pressure below one atmosphere. But an objection to this deduction is that the pressure of the minimum points of *pv* for other gases is higher than the critical, and if this were the case also for hydrogen, the critical pressure would have to be extremely low and very much beneath one atmosphere.

To examine the behaviour of hydrogen under as widely different conditions as possible, the author selected four different temperatures at which to work: the boiling point of water, 100°, the melting point of ice, 0°, the boiling point of liquid ethylene, —103·5°, and the boiling point of liquid oxygen, —182·4°. The pressures employed varied from 1 to 70 atmospheres. The apparatus, of which a sketch is given, was of very simple construction. The hydrogen was compressed in a bulb of known capacity having a capillary neck, and immersed in a bath kept at a fixed temperature. The volume was measured directly by transference to a eudiometer. Liquid oxygen used in cooling the gas was prepared by cooling down oxygen under pressure to the temperature of boiling ethylene (liquefied by means of ether and carbonic anhydride), and then suddenly releasing the pressure and allowing the cold produced by expansion to liquefy the gas.

For the three first of the above four fixed temperatures, the behaviour of hydrogen on compression is that already recorded: there is a constant increase of *pv*, with pressures rising from 1 to 70 atmospheres. The curves expressing the relation between *p* and *pv*, all three have their concave sides turned towards the axis of *p*. The following three empirical equations are found to express the behaviour of hydrogen under these conditions:—

$$\begin{array}{llrl}
(1) & \text{At} & 99{\cdot}14^\circ & pv = 1{\cdot}361299 + 0{\cdot}001360051p - 0{\cdot}000004099p^2. \\
(2) & ,, & 0^\circ & pv = 0{\cdot}997393 + 0{\cdot}001308924p - 0{\cdot}000004257p^2. \\
(3) & ,, & -103{\cdot}5^\circ & pv = 0{\cdot}6187044 + 0{\cdot}00087512p - 0{\cdot}0000026916p^2.
\end{array}$$

At the fourth temperature, however, that of boiling oxygen, —182·4°, a very important change is found to have taken place. For here, for pressures up to 14 atmospheres, *pv decreases* with rising pressure; at about 14 atmospheres a minimum occurs and from this point *pv* again begins to rise and to increase continually with the pressure. The observations in this case from 16 to 70 atmospheres may be expressed by—

$$(4)\ pv = 0{\cdot}3322739 + 0{\cdot}0002599317p + 0{\cdot}0000003091856p^2.$$

It therefore appears from the above that the behaviour of hydrogen at the boiling point of oxygen is perfectly similar to that of other gases at the ordinary temperature, pv first decreasing to a minimum and afterwards increasing with rising pressure.

The results expressed in the above four equations may also be represented by the following general empirical equation:—

$$p = \frac{\mathrm{RT}}{v - \alpha} - \frac{\mathrm{K}}{\epsilon^{\mathrm{T}} v^2},$$

where T is the absolute temperature, $\mathrm{R} = 1/273$, $\alpha = 0{\cdot}00111665$, $\mathrm{K} = 0{\cdot}00051017$, and $\epsilon = 1{\cdot}003892$. From this equation, the values for T, p, and v in the critical state can be obtained by differentiating p with regard to v, and equating to zero. We get in this way in the critical state $\mathrm{T}\epsilon^{\mathrm{T}} = 8\mathrm{K}/27\mathrm{R}\alpha$; $\mathrm{P} = \mathrm{RT}/8\alpha$ and $\mathrm{V} = 3\alpha$. This gives—

	Critical temperature........	32·6 or −240·4°.
	„ pressure...........	13·3 atmospheres.
	„ volume............	0·00335.
whence	„ density...........	0·327.

Hence it appears that the critical temperature of hydrogen is excessively low, very much beneath that of any other gas, and also that hydrogen has a very low critical pressure.

It is this very low critical temperature, combined with a low critical pressure, that serves to explain the apparent exception of hydrogen at the ordinary temperature from the behaviour of other gases on compression. According to Van der Waals all gases in the critical state behave exactly alike, and are in strictly comparable conditions. These comparable conditions may be retained for states other than the critical, if, instead of expressing temperature, pressure, and volume in terms of the ordinary units, the critical temperature, pressure, and volume be each taken as unity, and gases then compared under conditions which are similar in terms of these units. All gases are then found to behave alike, and the curve expressing the relation between any two properties will be one and the same for all gases.

The author constructs the curve representing the relation between the temperature and pressure (in units of the critical) of the minimum points of pv as observed for different gases. This curve is of course one and the same for all gases, and, as the author has already shown, is the continuation of the curve for the vapour-tensions of the liquefied gases. The observations used for constructing it are chiefly those of Amagat, and are for the gases carbonic anhydride, ethylene, methane, oxygen, and nitrogen. It is found that from the point where critical temperature and pressure are each unity, the curve rapidly rises until when the pressure is about 3·1 and the temperature 1·4, a maximum is reached. From this point the curve again falls, and when the temperature is about 2·7, the pressure of the minimum points of *pv* has fallen again to the critical pressure, and is still rapidly falling.

To apply this to hydrogen, the critical temperature of which is 32·6 and the critical pressure 13·3 atmospheres. The pressure of the minimum point of *pv* for a temperature of 1·4 times the critical temperature, is about 3·1 times the critical pressure, but from this point the pressure of the minimum of *pv* continues to fall. Thus when the temperature is 2·7 times the critical, or about −185°, the pressure of the minimum point of *pv* is only equal to the critical pressure or 13·3 atmospheres, and by observation at −184·4° the pressure of this point was found to be about 14 atmospheres, a very close approximation. From this point the pressure of the minimum of *pv* continues to fall rapidly, and at length, becoming a small fraction of the critical, falls in the case of hydrogen below one atmosphere, and at temperatures still comparatively low no longer comes under observation. It will be seen that this process is really brought about by hydrogen having a very low critical temperature. combined with a very low critical pressure.

The exception observed in the behaviour of hydrogen on compression is, then, only an apparent one, hydrogen as a matter of fact behaving as all other gases.

In a note at the end Zakrzewski, who communicates this paper, gives brief details of attempts which the author had made towards liquefying hydrogen. The gas, compressed to 110 atmospheres, was cooled by means of liquid nitrogen to −213·8°. By suddenly releasing the pressure as low a temperature as −223° was obtained, but without any signs of liquefaction. H. C.

Simple Diffusion Experiment. By M. W. BEYERINCK (*Zeit. physikal. Chem.*, **3**, 110—112).—When a drop of acid is let fall on a surface of gelatin, a visible depression is formed on the surface at the edge of the drop, and this depression moves outwards as the acid diffuses. Hence it is possible to determine the rate of diffusion of an acid on a gelatin plate by measuring the rate of motion of this depression. H. C.

Raoult's Law of Freezing. By R. FABINYI (*Zeit. physikal. Chem.*, **3**, 38—45).—It is a well-known fact that the presence of impurity or admixture of foreign material lowers the melting point of any solid substance. The author has examined this lowering of the melting point in the case of naphthalene, and finds that it follows exactly similar laws to those discovered by Raoult for the reduction of the freezing point of solutions. Thus by mixing various substances in different proportions with naphthalene, and determining the melting points of the mixtures, it is found that the reduction of the melting point is proportional to the amount of foreign substance present, and is constant for equimolecular proportions.

A description of the apparatus used is given, as also the results of a number of determinations. From these latter, it appears that compounds of the most different constitution which do not contain a carboxyl-group, and themselves melt at from 37° to 273°, when mixed in the proportion of 1 mol. to 100 mols. $C_{10}H_8$, cause a reduction of the melting point of 0·60° to 0·65°. If 2 mols. per 100 be taken, double, if 3 mols., treble the above reduction is obtained. Acids, on the other hand, containing a carboxyl-group give only half the above depression in each case, so that 4 mols. of an acid become equal to only 2 mols. of a compound containing no carboxyl in this respect. H. C.

Raoult's Law of the Reduction of the Freezing Point. By J. F. Eykman (*Zeit. physikal. Chem.*, 3, 113—114).—The molecular reduction of the freezing point of phenol was found by the author to be about 76, a number agreeing with that calculated by the Van't Hoff formula (Abstr., 1888, 780), but differing from that found by Raoult, 58·3, in his experiments. As the number given by Raoult for the molecular reduction of the freezing point of naphthalene is 82, whereas according to the Van't Hoff formula it should be 69·4, the author has also made a series of determinations, using naphthalene as a solvent. The number obtained for the molecular reduction is in very fair agreement with that calculated by Van't Hoff. H. C.

Molecular Depression of the Freezing Point of Benzene by Iodoform. By E. Paternò (*Ber.*, 22, 465—466).—Raoult (*Ann. Chim. Phys.* [6], 2, 88) found that the lowering of the freezing point of benzene produced by iodoform indicated that the latter had a molecular weight double that which is generally accepted. The author gives in tabular form the results of seven experiments on the lowering of the freezing point of benzene by quantities of iodoform varying from 1·2161 to 10·5385 parts in 100 parts of benzene. The maximum molecular depression was found to be 61·46 with 1·2161 parts of iodoform, the minimum 54·76 in the two experiments with 3·5919 and 3·6561 parts of iodoform respectively. The freshly prepared solutions are light-yellow, but almost immediately become brown, an indication of partial decomposition. It was found, however, by two experiments that the freezing point of the solutions underwent no perceptible alteration after 6, or even after 24, hours.

The depression produced by iodoform must therefore be looked on as normal, and although the values found actually differ from the normal, this fact simply proves that partial decomposition takes place.

F. S. K.

Molecular Volumes of Liquids. By H. Kopp (*Annalen*, **250**, 1—117).—This lengthy communication contains a *résumé* of much of the work that has been done up to the present on the molecular volumes of liquids. It is chiefly devoted to a comparison of the molecular volumes at the boiling points, and at any fixed temperature, say, 0°, and to showing that the first alone bring out definitely those relations which exist between the molecular volume and chemical composition.

H. C.

Action of Ferments. By G. Tamman (*Zeit. physikal. Chem.*, 3, 25—37).—The action of emulsin on amygdalin, salicin, and urea, and also the action of invertin on cane-sugar, were studied. At 0° and at the boiling point of water the action of the ferment is in each case at a minimum, but between these temperatures there is a point of maximum action. At no temperature, however, is the action a complete one, although the author shows that the changes do not belong to the class of reversible reactions, and therefore do not lead to any conditions of equilibrium.

The end of the reaction is conditioned by temperature and the concentration of the solution. Thus, at temperatures as under, the following percentage amounts of amygdalin are decomposed in a 30 c.c. solution containing 0·51 gram of amygdalin and 50 milligrams of emulsin.

t	10°	15°	32°	46°	65°	72°
p	15	16	24	32	20	5

Increasing the amount of the ferment increases also the amount of decomposition up to a certain point, but beyond this has no further action, or may even decrease the amount decomposed. By adding the products of decomposition to the solution, the action of the ferment is weakened, and in a solution, the composition of which already corresponds with the end condition for the given temperature, the ferment refuses to act at all.

The actions of ferments are also studied as time reactions, and the results plotted in curves. These show that they do not follow the course of other catalytic actions, which can generally be represented by logarithmic curves, but obey more complicated laws. In this respect the action of invertin on cane-sugar and of yeast on grape-sugar, which were studied, appear to be very similar. No general rules are deduced.

H. C.

Numerical Relations of the Atomic Weights. By S. STRANSKY (*Monatsh.*, **10**, 19—25).—A number of numerical relations among the atomic weights, more particularly of allied elements, are pointed out. Among others, the following two relations are given:—(1.) The atomic weights of elements of any natural group are rational multiples of that of the first member of the series, minus a constant or some number regularly increasing in arithmetical progression. (2.) The atomic weights of elements of any natural group are rational multiples also of the second member of the series, minus a constant or some number regularly increasing in arithmetical progression. A number of tables illustrating these and other relations are given. H. C.

Lecture Experiments. By A. ALESSI (*Ber.*, **22**, 485—486).—The composition and the most important reactions of hydrogen chloride and other gases can be demonstrated as follows:—One or more small, thin, sealed bulbs, containing mercuric oxide, are placed in a strong glass flask, which is then filled with dry hydrogen chloride, closed with the thumb, and shaken until the bulbs are broken. The oxide is converted into chloride, and on opening the flask under mercury the latter completely fills the vessel. The reaction between sodium and hydrogen chloride can be shown in like manner by using sealed bulbs filled with sodium amalgam; on opening the flask under water the liquid rises and occupies half the volume, and the residual gas can be shown to consist of hydrogen. To demonstrate that hydrogen chloride contains chlorine, lead dioxide is employed; on breaking the bulbs, the brown oxide is converted into chloride, which appears moist, owing to formation of water. The flask is then opened under water, and the residual chlorine, occupying one quarter of the original volume, can be readily recognised.

To show that nitrogen and a halogen acid are formed by the action of chlorine or bromine on ammonia, the bulbs are filled with very concentrated aqueous ammonia, and, after the experiment, the flask is opened under water or dilute acid, when the liquid rises and occupies two-thirds of the volume of the vessel. The action of ammonia on hydrogen chloride and of hydrogen sulphide on metallic salts can be shown in like manner.

F. S. K.

Inorganic Chemistry.

Absorption of Hydrogen by Metals. By M. THOMA (*Zeit. physikal. Chem.*, **3**, 69—102).—Palladium charged with hydrogen electrolytically, expands and increases in volume equally in all directions. A contraction takes place on removing the hydrogen, which is greater than the previous expansion, but if the palladium is successively charged and discharged the contraction lessens in amount, not, however, with any definite regularity. Only a certain amount of hydrogen can be permanently retained, for palladium charged with hydrogen beyond a certain limit parts with the gas spontaneously. Below this limit of saturation, the expansion is proportional to the amount of hydrogen absorbed, but on passing the limit the expansion increases more rapidly than the absorption. The hydrogen retained above the limit of saturation is therefore less dense than that retained below. All hydrogen retained above the saturation point is given off when the palladium is left to itself again, and a contraction takes place equal to the expansion due to supersaturation. The supersaturation is dependent in amount very largely on the strength of the current employed. The hydrogen was found to have diffused in the palladium in one half hour to a distance of 4 to 5 mm. from the surface of attack.

Iron is also readily supersaturated with hydrogen. This takes place whenever iron comes in contact with dissociated hydrogen, either in the voltameter or that which is being generated on its own surface by the action of an acid. From the surface of the supersaturated iron, hydrogen is again spontaneously liberated, and the amount obtained is proportional to the extent of surface.

H. C.

Action of Sulphurous Acid on Sodium Thiosulphate. By A. VILLIERS (*Compt. rend.*, **108**, 402—403).—The salt to which the author attributed the composition $Na_2S_4O_8$ really contains four atoms of hydrogen, and is hydrated sodium tetrathionate, $Na_2S_4O_6 + 2H_2O$. The percentage amounts of sodium and sulphur corresponding with the two formulæ are almost identical. It follows that the only products of the interaction of sodium thiosulphate and sulphurous acid are sodium trithionate and tetrathionate.

The reaction is precisely similar with the potassium salt, but in this case the trithionate is the less soluble of the two products, and if the first crop of crystals is dissolved in hot water and the hot liquid mixed with alcohol, the trithionate separates in the anhydrous condition on cooling. C. H. B.

Preparation of Nitrous Oxide. By G. CAMPARI (*Chem. Centr.*, 1888, 1569, from *Ann. Chim. Farm.*, **8**, 253—255).—5 parts of stannous chloride, 10 parts of hydrochloric acid, sp. gr. 1·21, and 0·9 part of nitric acid, sp. gr. 1·38, are heated to boiling, when the evolution of nitrous oxide commences, and it continues to be evolved quite regularly and in a pure state. The above proportions of the ingredients should be adhered to, as otherwise the gas is evolved irregularly, and even with violent explosions. J. W. L.

Sodium Phosphite. By L. AMAT (*Compt. rend.*, **108**, 403—405).—By dissolving phosphorous acid in a large excess of sodium hydroxide and treating the product with alcohol, Zimmermann obtained an oily liquid, which he regarded as containing trisodium phosphite, Na_3PO_3, but from which he obtained no crystals. The author finds that if phosphorous acid is dissolved in sodium hydroxide in such proportion that the liquid contains the two compounds in the proportion $Na_2HPO_3 + 27NaOH$, and this solution is evaporated slowly in a vacuum, crystals separate which have the composition $Na_2HPO_3 + 5H_2O$. If a similar solution is treated with alcohol until the latter removes no more sodium hydroxide, the product is the same salt. When absolute alcohol is used, water is removed as well as sodium hydroxide, and the final product is a supersaturated solution of the disodium phosphite, which readily crystallises. The same salt is obtained by adding 4 vols. of alcohol to the mother-liquor from the crystals obtained by evaporation.

From these results it follows that trisodium phosphite does not exist, and that phosphorous acid is bibasic, as Würtz contended. C. H. B.

The Acid Character of the Salts of the Heavy Metals. By B. LACHOWICZ (*J. pr. Chem.* [2], **39**, 99—106).—Several organic bases give precipitates when shaken with aqueous solutions of salts of the heavy metals (Lachowicz and Bandrowski, Abstr., 1888, 1281); in the table (p. 570) the sign + denotes that such a precipitate is formed between the corresponding base and salt.

When the heats of formation (Thomsen's) of the salts in this table are compared, it is found that for salts of the same acid the lower the heat of formation the greater is the capability of combining with organic bases, and for salts of the same metal, the greater the heat of formation the greater is the capability of combining with organic bases.

The author explains this by supposing that when a metal forms a salt with an acid, the "energy" of the acid radicle will be more or less neutralised according as the heat of formation is greater or

	Amines of the paraffins.	Piperidine, pyridine, quinoline.	Aniline.	Toluidine.	Methylaniline.	Dimethylaniline.	β-Naphthylamine.	α-Naphthylamine.	Diphenylamine.
$Zn(NO_3)_2$	+	+							
$ZnSO_4$	+	+	+						
$ZnCl_2$	+	+	+	+					
$Pb(NO_3)_2$ $Cu(NO_3)_2$	+	+	+	+	trace	trace			
$CuSO_4$	+	+	+	+	+		+		
$HgCl_2$	+	+	+	+	+	trace	+		
$CuCl_2$	+	+	+	+	+	trace	+	trace	
$AgNO_3$	+	+	+	+	+	+	+	+	

less; thus in potassium chloride (K_2,Cl_2 = 211220 cal.) the residual "energy" of the Cl is much less than in cupric chloride (Cu,Cl_2 = 51640 cal.), and still less than in hydrochloric acid (H,Cl = 44002 cal.); so that potassium chloride shows less tendency to combine with organic bases than cupric chloride, and this last less than hydrochloric acid.

The physiological action of the salts of the heavy metals may also be referred to the residual "energy" of their acid radicles, and thus depends on the heats of formation of the salts. A. G. B.

Properties of the Mercurammonium Chlorides. By G. André (*Compt. rend.*, **108**, 233—236 and 290—293).—The solutions employed contained 33·875 grams of mercuric chloride and 4·25 grams of ammonia respectively per litre, and the compounds were obtained by precipitation in the cold.

When equal volumes of the two solutions are mixed, and the precipitate is collected after several hours or days, washed with a small quantity of water, and dried at 110°, it has not exactly the composition of mercurammonium chloride, NH_2HgCl. This result is due to the decomposing action of the water, which at once becomes evident in dilute solutions, and which, as Kane has shown, results ultimately in the formation of Millon's dimercurammonium chloride, $NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$. If, however, mercuric chloride is added to an excess of ammonia and the precipitate is washed rapidly with a small quantity of water, the compound NH_2HgCl is obtained in a pure condition. The presence of Millon's compound in the precipitates formed in dilute solutions is readily detected by the fact that after these precipitates have been dried at 110°, they evolve water, if heated at a higher temperature.

With solutions of the strengths given above, the precipitate after one hour contained 0·11 mol., after 12 days 0·25 mol. of Millon's compound for each molecule of mercurammonium chloride. With 6 mols. of ammonia to each molecule of mercuric chloride, decomposition proceeds further, and the precipitate contains the two compounds in equal molecular proportions. With an increasing amount of ammonia, the precipitate eventually consists solely of the compound $NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$. Variations in the proportion of mercuric chloride have no influence on the composition of the precipitate.

If the two solutions are mixed in equal proportions, allowed to remain 24 hours, the liquid decanted off, the precipitate treated with 8 vols. of the ammonia solution, and this treatment repeated after a second 24 hours, the final product consists entirely of Millon's compound, whereas the original precipitate contained only 25 per cent. of it. If the solutions are mixed in equal proportions, allowed to remain 24 hours, the liquid decanted off, 4 vols. of water added to the precipitate, and this treatment repeated twice at intervals of 48 hours, the product has the composition $NH_2HgCl,3NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$. Direct experiments with equal volumes of the solutions, and using equal volumes of water for washing, showed that the decomposing action of the water diminishes as the concentration of the ammonia increases. Ammonium chloride acts in exactly the opposite way to water. The addition of 1 vol. of the mercuric chloride solution to 5 vols. of the ammonia solution gives a precipitate which consists almost entirely of Millon's compound; but if after 24 hours the liquid is decanted off and the precipitate is treated with 2 vols. of a solution of ammonium chloride of similar strength, and allowed to remain for two days with occasional agitation, the precipitate is completely converted into the compound NH_2HgCl. The proportion of ammonium chloride required to produce this result is smaller the smaller the quantity of dilute ammonia used in the precipitation. The addition of ammonium chloride without previously decanting the liquid from the precipitate has very little effect upon the latter. C. H. B.

Valency of Aluminium. By A. COMBES (*Compt. rend.*, **108**, 405—408).—Aluminium acetonylacetonate, $nAl(C_5H_7O_2)_3$, is a white solid which melts at 193—194°, and boils without decomposition at 314—315°. Its vapour-density as determined by V. Meyer's method at the boiling point of mercury is 11·25, which corresponds with a molecular weight of 324·8. The calculated molecular weight of the compound $Al(C_5H_7O_2)_3$ is 324·5. The evolution of gas was regular, and there was no evidence of any decomposition. It follows that at a temperature only 45° above the boiling point of the compound, molecules of the type $Al_2(C_5H_7O_2)_6$ have no existence. Whilst accepting the evidence of the existence of molecules of the formula Al_2Cl_6 at comparatively low temperatures, the author considers that the great mass of the evidence at present accumulated shows that aluminium is really trivalent. C. H. B.

Hydrogen Peroxide and Chromic Acid. By BERTHELOT (*Compt. rend.*, **108**, 477—479).—When hydrogen peroxide is mixed with potassium dichromate, and an excess of dilute ammonia is added immediately, a chamois-yellow precipitate is formed, which contains hydrogen peroxide, chromic oxide, and chromic anhydride. If the liquid is decanted off, and the precipitate is washed with water, the first washings are colourless, but succeeding washings are yellow and contain chromic acid. A certain quantity of free oxygen is also evolved, and it is evident that the precipitate is unstable, and gradually decomposes with reoxidation of the chromic oxide. It probably has the composition $n\mathrm{CrO_3,Cr_2O_3,3H_2O_2}$. A similar and probably identical precipitate is obtained when hydrogen peroxide is added to potassium hydroxide containing freshly precipitated chromic hydroxide in suspension. The same precipitate is formed if hydrogen peroxide is added to potassium dichromate containing chromic hydroxide in suspension; the green precipitate becomes yellow, and dissolves completely on addition of potassium hydroxide. The solution at first has the greenish tint observed when hydrogen peroxide is added to normal potassium chromate, but this gradually disappears.

This precipitate is the intermediate compound to which reference has been made in the author's previous papers (this vol., pp. 350 and 468). C. H. B.

Titanium Peroxide. By L. Lévy (*Compt. rend.*, **108**, 294—296). —The composition of the product of the action of hydrogen peroxide on titanic oxide has been variously stated by different authors. The want of agreement between their results is due to the fact that the action of the hydrogen peroxide is very slow, and the precipitate decomposes while being dried. As no known method of solution or precipitation permits of the separation of the peroxide from an excess of either constituent, the author endeavoured to determine the composition of the product by a method of approximation. A solution of hydrogen peroxide of known strength was mixed with definite quantities of a solution of titanic oxide in sulphuric acid. After a long time, the mixtures were examined in order to ascertain which of them still contained hydrogen peroxide. A first approximation pointed to a formula between $\mathrm{TiO_3}$ and $\mathrm{Ti_2O_7}$, a second to a formula between $\mathrm{TiO_3}$ and $\mathrm{Ti_5O_{16}}$, and a third to a formula between $\mathrm{TiO_{2\cdot98}}$ and $\mathrm{TiO_{3\cdot04}}$. In all probability the formula is $\mathrm{TiO_3}$, but these experiments only show that titanic oxide forms a peroxide at the expense of the hydrogen peroxide, and any one of the three formulæ, $\mathrm{TiO_2}$; $\mathrm{TiO_2,H_2O_2}$; $\mathrm{Ti_2O_5,H_2O_2}$, agrees with the result. The composition of the higher chloride, and the existence of additive compounds of the oxyfluoride $\mathrm{TiO_2F_2}$ and alkaline fluorides, afford additional evidence in favour of the formula $\mathrm{TiO_3}$.

Hydrogen peroxide or the titanium peroxide decolorises phenolphthaleïn, and hence if the acid solution of titanic oxide is titrated after addition of hydrogen peroxide its acidity seems to be increased. C. H. B.

Amorphous Bismuth. By F. Hérard (*Compt. rend.*, **108**, 293).—Amorphous bismuth can be obtained in the same way as amorphous antimony (Abstr., 1888, 1256) by heating ordinary bismuth to bright redness in a current of nitrogen. Hydrogen and carbonic oxide will not give the same result. The product contains 99·6 per cent. of bismuth and 0·4 per cent. of oxygen. The presence of bismuth oxide explains the high melting point 410°, but not the low sp. gr. 9·483. The amorphous bismuth is more readily attacked by reagents than the crystallised metal; in nitric acid it dissolves almost instantly. C. H. B.

Non-magnetisable Alloys of Palladium suitable for the Manufacture of Watches. By C. A. Paillard (*Dingl. polyt. J.*, **270**, 143).—The use of alloys of the following composition is recommended:—

	Pd.	Cu.	Fe.	Ag.	Au.	Pt.	Ni.
I.	60—75	15—25	1—5	—	—	—	—
II.	50—75	20—30	5—20	—	—	—	—
III.	65—75	15—25	1—5	3—10	1—2·5	0·05—2	1—5
IV.	45—50	15—25	2—5	20—25	2—5	2—5	2—5

Alloy I is obtained by mixing half the palladium with the remaining metals, fusing the mixture with borax and powdered charcoal, adding the remainder of the palladium, again fusing and pouring the mass into suitable moulds. II is a cheaper alloy and useful for common watches and certain parts of the works. Alloy III is not affected by atmospheric changes, its elasticity is not influenced by temperature, while its astatic properties are even greater than those of alloys I and II. Alloy IV, besides exhibiting all the properties of the former, is characterised by its great hardness. D. B.

Mineralogical Chemistry.

Palæopicrite from Stoppenberg, near Thale, in the Harz. By K. A. Lossen (*Chem. Centr.*, 1889, 58, from *Zeit. deut. geol. Gesell.*, **40**, 372—373).—Palæopicrite occurs in a palæozoic slate of the diabase family with much serpentinised olivine, and some plagioclase, hornblende, diabase-augite, and ilmenite. An analysis gave the following result:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
38·35	0·90	7·03	6·82	6·68	25·69	0·12	0·40	0·45

H_2O.	P_2O_5.	TO_3(?).	Sp. gr.
10·89	0·12	0·22	2·7297

J. W. L.

Monazite as an Accessory Constituent of Rocks. By O. A. Derby (*Amer. J. Sci.*, **37**, 109—113).—Some years ago the author's attention was called to a peculiar, heavy, yellow sand, from the province of Bahia, Brazil, which proved to consist of monazite containing 28·7 per cent. of phosphoric anhydride, 31·3 per cent. of cerium oxide, and 39·9 per cent. of didymium and lanthanum oxides. The sand occurs in considerable batches on the sea shore near Alcobaça, where it seems to have been concentrated by wave action. Monazite has since been found to be widely distributed in the sea- and river-sands of Brazil. As gneiss is the only rock that is at all abundant in the vicinity of Rio de Janeiro, it was thought that the monazite might come from that rock. All the tests made on gneiss, granite, and syenite have given, in addition to zircon, microscopic crystals of a heavy, yellow mineral which is undoubtedly monazite. The basic eruptive rocks examined have afforded no trace of this mineral. In all these tests, care was taken to select samples representing the principal mass of the rock free from veins and mineral aggregates. The rock, found to be richest in monazite, was a fine-grained granitite exposed near Rio de Janeiro. This rock contains 0·07 per cent. of monazite in fine grains. This percentage includes a small amount of zircon that could not be completely separated.

B. H. B.

Meteorites of Shalka and Manbhoom. By H. B. v. FOULLON (*Chem. Centr.*, 1889, 270, from *Ann. Naturh. Hofmus. Wien.*, **3**, 195—208).—The author has made several analyses of parts of these meteorites. Of that from Shalka in Bengal, the analysis of the chrom-ironstone contained in it (I), the complete analysis of a piece of the meteorite (II), and an analysis of bronzite also occurring in it (III and IV) are given.

	SiO_2.	Cr_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.	Na_2O.	S.	Fe.	P.
I.	—	56·82	26·14	11·36	—	5·68	—	—	—	—
II.	52·51	1·25	16·81	0·66	0·89	28·35	0·22	0·14	0·25	trace
III.	43·28	—	26·87	—	—	29·85	—	—	—	—
IV.	44·03	—	26·12	—	—	29·85	—	—	—	—

Of the Manbhoom meteorite the author gives the following analyses: I. The nickel-iron; II. The portion of the meteorite soluble in hydrochloric acid, which amounted to 63·91 per cent.; III. The portion insoluble in hydrochloric acid.

	SiO_2.	Fe_2O_3.	Cr_2O_3.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.
I.	—	—	—	—	—	—	—	—	—
II.	19·91	—	trace	0·09	16·52	0·07	19·33	0·40	—
III.	20·21	0·83	0·55	1·71	4·01	trace	7·37	1·53	0·44

	K_2O.	Fe.	Ni.	S.	P.
I.	—	1·26	0·49	1·70	0·20
II.	—	2·98	0·42	—	—
III.	0·20	—	—	—	—

J. W. L.

Organic Chemistry.

The Hydrocarbon $C_{60}H_{122}$. By C. Hell and C. Hägele (*Ber.*, **22**, 502—505).—The hydrocarbon $C_{60}H_{122}$ is obtained when myricyl iodide, prepared from the alcohol by Pieverling's method (this Journal, 1877, i, 586), is carefully heated at 130—140° with about one-tenth of its weight of finely divided potassium or sodium; the crude product is boiled with water, alcohol, light petroleum, and glacial acetic acid consecutively, and then repeatedly recrystallised from benzene, and boiled with light petroleum. It is a colourless powder, melting at 101—102°, very sparingly soluble in hot alcohol and ether, rather more easily in light petroleum and glacial acetic acid, but most readily in chloroform and benzene. It is partially decomposed when distilled under diminished pressure, yielding a hydrocarbon which melts at 69—70°, and is readily soluble in light petroleum.

F. S. K.

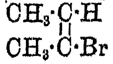
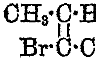
Propyl and Isopropyl Fluorides. By M. Meslans (*Compt. rend.*, **108**, 352—354).—These compounds were obtained by the action of the alkyl iodides on silver fluoride. The reaction takes place at the ordinary temperature, but more readily at about 50°, and is more energetic in the case of the isopropyl-derivative.

Propyl fluoride is a colourless gas with an ethereal odour and sweet burning taste. It burns with a luminous flame, with formation of hydrofluoric acid; when dry it has no action on glass or mercury. At +2°, under atmospheric pressure, it forms a very mobile, colourless liquid which has no action on glass. The gas is very soluble in alcohols, benzene, ether, and the alkyl iodides, and dissolves in its own volume of water at 16°. Its vapour-density at 20° is 2·161 (calc. 2·175).

Isopropyl fluoride is very similar to the preceding compound, but has a more pungent smell. It is very soluble in benzene, ether, and the alkyl iodides. Water at 15° dissolves 1·5 vols. of the gas; isopropyl iodide dissolves 70 vols.; ethyl alcohol at 16°, 27 to 30 vols. It liquefies at −5° under ordinary pressure; at 10° under a pressure of 2·5 atmos., and at 18° under a pressure of 3 atmos. It is very stable, and is not affected when heated for some time with a dilute solution of potassium hydroxide in a sealed tube at 100°.

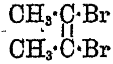
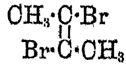
Iodine has very little action on isopropyl fluoride, but if the gas is passed into bromine at 30°, a colourless liquid is obtained which has a pleasant, piquant odour, and boils without decomposition at 143°. Isopropyl fluoride combines readily with chlorine at 10°, and yields a liquid which readily dissolves both gases. If an excess of the fluoride is used, and the excess is expelled by gently heating, the product is a colourless liquid which boils without decomposition at 105°, has a pleasant odour, and burns with a flame with a green edge, hydrogen fluoride being formed. C. H. B.

Brominated Derivatives of Pseudobutylene. By O. Hölz (*Annalen*, **250**, 230—240).—Pseudobutylene dibromide, prepared by passing pure pseudobutylene into bromine, boils at 156—158°, and is decomposed by an alcoholic solution of potassium hydroxide, yielding *monobromopseudobutylene*, $CH_3\cdot CBr{:}CH\cdot CH_3$. This liquid boils at 87—88°, and is slowly converted into crotonylene by treatment with an alcoholic solution of sodium ethoxide at 130°. The hydrocarbon is a mobile liquid boiling at 17—18°. If it is rapidly shaken with three times its volume of concentrated hydrobromic acid, and the mixture left at 0° for an hour, then diluted with water, and the oily product purified by distillation, *crotonylene hydrobromide*, the geometrical isomeride of monobromopseudobutylene, is obtained as a colourless liquid boiling at 83—84°. By using a larger proportion of hydrobromic acid, ethylmethylcarbin dibromide, $CEtMeBr_2$, is formed. It boils at 144—145°, and is decomposed by water at 160°, yielding ethyl methyl ketone.

As crotonylene hydrobromide is much more readily attacked by an alcoholic solution of sodium ethoxide than monobromopseudobutylene, these compounds have respectively the formulæ  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\; \| \\ CH_3\cdot C\cdot Br\end{array}$ and  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\; \| \\ Br\cdot C\cdot CH_3\end{array}$.

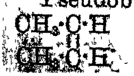
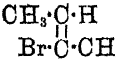
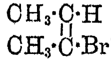
Crotonylene dibromide, $CMeBr{:}CMeBr$, is formed by adding bromine very slowly to well-cooled crotonylene. It boils at 146—147° with slight decomposition.

Isocrotonylene dibromide is prepared by treating the product of the action of bromine on monobromopseudobutylene with alcoholic sodium ethoxide. It boils at 149—150°.

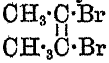
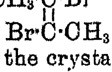
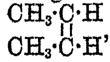
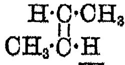
As crotonylene dibromide is more readily attacked by zinc-dust than isocrotonylene dibromide, the constitution of these compounds may be represented by the formulæ  $\begin{array}{l}CH_3\cdot C\cdot Br\\ \quad\;\; \| \\ CH_3\cdot C\cdot Br\end{array}$ and  $\begin{array}{l}CH_3\cdot C\cdot Br\\ \quad\;\; \| \\ Br\cdot C\cdot CH_3\end{array}$ respectively. Crotonylene dibromide unites with bromine, forming a crystalline tetrabromide which is converted into isodibromopseudobutylene by the action of zinc-dust. W. C. W.

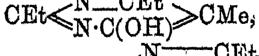
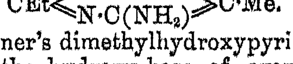
Conversion of Crotonylene Hydrobromide into Bromopseudobutylene. By M. PÜCKERT (*Annalen*, **250**, 250—251).—Crotonylene dibromide, from angelic dibromide, unites with bromine in carbon bisulphide solution, forming tribromobutane. Zinc-dust acts energetically on the alcoholic solution of trichlorobutane, yielding isobromopseudobutylene boiling at 86—88°. This compound is less readily attacked by an alcoholic solution of sodium ethoxide than crotonylene hydrobromide. W. C. W.

Arrangement of Atoms in Space. Part IV. By J. WISLICENUS (*Annalen*, **250**, 224—230, and 251—254).—The results of the experiments of Hölz and Pückert confirm the accuracy of the author's speculations on the constitution of tiglic and angelic acids.

Pseudobutylene boiling at 1—3° is represented by the formula  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\; \| \\ CH_3\cdot C\cdot H\end{array}$. Pseudobutylene forms a dibromide, from which isobromopseudobutylene,  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\, \|\\ Br\cdot C\cdot CH_3\end{array}$, is easily prepared. Crotonylene hydrobromide or monobromopseudobutylene,  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\;\, \|\\ CH_3\cdot C\cdot Br\end{array}$, is the geometrical isomeride of the preceding compound. Both substances unite with bromine to form $\beta\gamma_2$-tribromobutane, $CH_3\cdot CHBr\cdot CBr_2\cdot CH_3$, and with hydrogen bromide, forming ethylmethylcarbin dibromide,

$$CH_3\cdot CH_2\cdot CBr_2\cdot CH_3.$$

Crotonylene unites with bromine to form $\beta\gamma$-dibromopseudobutylene,  $\begin{array}{l}CH_3\cdot C\cdot Br\\ \quad\;\;\, \|\\ CH\cdot{}_3C\cdot Br\end{array}$ (b. p. 147°), and $\beta\gamma_2$-tribromobutane yields isodibromopseudobutylene,  $\begin{array}{l}CH_3\cdot C\cdot Br\\ \quad\;\;\, \|\\ Br\cdot C\cdot CH_3\end{array}$ (b. p. 150°). Both compounds unite with bromine, forming the crystalline crotonylene tetrabromide. As treatment with a solution of sodium carbonate converts tiglic dibromide into crotonylene hydrobromide, and angelic dibromide into isobromopseudobutylene, the author hopes to eliminate HBr and CO_2 from the hydrobromides of tiglic and angelic acids, and in this way obtain pseudobutylene,  $\begin{array}{l}CH_3\cdot C\cdot H\\ \quad\;\;\, \|\\ CH_3\cdot C\cdot H\end{array}$, and isopseudobutylene,  $\begin{array}{l}\;\;\, H\cdot C\cdot CH_3\\ \quad\;\;\, \|\\ CH_3\cdot C\cdot H\end{array}$, respectively.
W. C. W.

Constitution of Cyanethine and its Analogues. By E. v. Meyer (*J. pr. Chem.* [2], **39**, 156).—Cyanethine and its analogues are probably diazines. The hydroxy-base of cyanethine can be obtained by the condensation of equal mols. of propionamidine and ethyl α-propiopropionate; it is therefore *hydroxymethyldiethylmetadiazine*,  $CEt\!\begin{array}{l}\diagup N{\equiv}CEt\diagdown\\ \diagdown N\cdot C(OH)\diagup\end{array}\!CMe$, and cyanethine is *amidomethyldiethylmetadiazine*,  $CEt\!\begin{array}{l}\diagup N{\equiv\!\equiv}CEt\diagdown\\ \diagdown N\cdot C(NH_2)\diagup\end{array}\!C\cdot Me$.

Pinner's dimethylhydroxypyrimidine (Abstr., 1886, 46) is identical with the hydroxy-base of cyanmethine (Abstr., 1883, 653; 1884, 1292).
A. G. B.

Polymerides of the Nitriles: Dimolecular and Trimolecular Nitriles. By E. v. Meyer (*J. pr. Chem.* [2], **39**, 188—198; compare this vol., p. 114).—Dimolecular ethyl cyanide is imidopropionylethyl cyanide (this vol., p. 114); cyanethine is amidomethyldiethylmetadiazine (preceding Abstract).

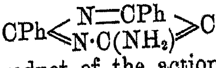
Imidobenzoylethyl cyanide, NH:CPh·CHMe·CN, is obtained when benzonitrile and ethyl cyanide (equal mols.) react with sodium in ether; a red mass is formed which, when treated with water, yields sodium hydroxide and the imido-compound, which is dissolved in ethyl acetate and precipitated by petroleum in the form of oblique, truncated prisms, melting at 97°.

α-Benzoylethyl cyanide, COPh·CHMe·CN, is formed when the above imido-compound is warmed with dilute hydrochloric acid. An oil is

the first product; this is dissolved in ether and dried over lime, when a liquid is left which has an unpleasant, aromatic odour, and gradually solidifies.

By the action of phosphorus pentachloride on α-propionylethyl cyanide (this vol., p. 114), a yellowish oil, boiling between 172° and 177°, is obtained. This has the formula C_6H_8ClN, and is probably $CEtCl\!:\!CMe{\cdot}CN$; potassium hydroxide decomposes it, evolving ammonia; hydrochloric acid at 150° acts on it, producing chiefly carbonic anhydride and diethyl ketone.

The author here replies to Hanriot and Bouveault (*Bull. Soc. Chim.*, **51**, 176), who have criticised his views on the constitution of dimolecular ethyl cyanide.

Amidomethyldiphenylmetadiazine,  $CPh\lessdot\genfrac{}{}{0pt}{}{N{=\!=}CPh}{N{\cdot}C(NH_2)}\gtrdot CMe$ (*cyandiphenylethine*), is obtained when the product of the action of sodium on ethyl cyanide is heated at 150° with an equal weight of benzonitrile in a sealed tube for three hours; the resulting mass is treated with ether and then with water, and the residue crystallised from alcohol; it melts at 172—173°, softening at 170°, and is sparingly soluble. The *sulphate* forms slender needles, and the *hydrochloride*, $C_{17}H_{15}N_3,HCl$, crystallises in prisms melting with decomposition at 238°. When the base is heated with strong hydrochloric acid, and water is added, *hydroxymethyldiphenylmetadiazine* is obtained (compare this vol., p. 114). This crystallises from hot alcohol in tufts of needles, sparingly soluble, and melting at 256°. Its *methyl*-derivative, $C_{17}H_{13}N(NMe)O$, forms prisms which melt at 121—122°.

Amidomethylethylisopropylmetadiazine, $C_{10}H_{17}N_3$, crystallises from weak alcohol in lustrous, seemingly rhombic laminæ melting at 153—154°. It is being further investigated. A. G. B.

Physical Properties of Methyl Alcohol. By W. DITTMAR and C. A. FAWSITT (*Trans. Roy. Soc. Edin.*, **33**, 509—534).—To purify crude methyl alcohol, 100 c.c. of the spirit is digested with 150 grams of powdered sodium hydroxide, after which it is distilled on a water-bath; 500 grams of oxalic acid crystals are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the alcohol, purified as above, is added, and the whole cautiously heated on a water-bath. The methyl oxalate thus obtained is thoroughly dried by pressure, and the alcohol regenerated by digestion with water at 70°. To dehydrate the alcohol thus obtained, digestion with baryta, lime, and dried copper sulphate is necessary. A very full account of the processes, successful and unsuccessful, is given, and of many operations performed and results obtained, which, although not finally employed, led the authors to adopt fresh measures and warned them against false results. In the estimation of tension it was found that air-free alcohol "bumped" seriously; consequently, it having been found that the error introduced by the employment of alcohol containing air was infinitesimal, the remaining densities, &c., were determined without freeing the alcohol from air. An abstract of the result of the vapour-tension determinations is given in the following table; in the original memoir, figures are given for every degree.

Table of Vapour-tension of Methyl Alcohol in Millimetrès of Mercury at 0°.

Temp.	Tension.	Temp.	Tension.	Temp.	Tension.
0°	29·7	30°	158·9	60°	624·3
10	53·8	40	259·4	64·96	760·0
20	94·0	50	409·4		

The methods, apparatus, and calculations employed in the estimation of the specific gravity are most fully detailed in a table, of which the following is an abstract, figures being given in the original for each percentage :—

Per cent. of $CH_3 \cdot OH$.	Sp. gr. at 0°.	Sp. gr. at 15·96°.	Per cent. of $CH_3 \cdot OH$.	Sp. gr. at 0°.	Sp. gr. at 15·96°.
0	999·87	999·07	60	909·17	897·98
10	984·29	982·62	70	886·87	874·87
20	972·33	968·08	80	863·14	850·35
30	960·57	953·67	90	837·51	823·96
40	945·7	936·97	100	810·15	795·89
50	928·73	918·55			

E. W. P.

Products of the Slow Combustion of Ethyl Ether. By L. Legler (*Chem. Centr.*, 1888, 1604).—The solid substance obtained by the author by the slow combustion of ethyl ether is *hexaoxymethylene peroxide*, $C_6H_{12}O_8,3H_2O$. When treated gradually with ammonia, *hexaoxymethylenediamine*, $C_6H_{12}O_6N_2$ is formed. The oxide is decomposed by alkalis into formic acid and hydrogen. With gaseous ammonia, it explodes ; with bromine water, it forms an orange-yellow precipitate, which gives off bromine when exposed to the air, with formation of *hexamethyleneamine dibromide*, $C_6H_{12}N_4Br_2$.

J. W. L.

Products of Alcoholic Fermentation, with Special Reference to the Formation of Glycerol. By V. Thylmann and A. Hilger (*Chem. Centr.*, 1889, 260; from *Arch. Hygiène*, 8, 451—467).—From a series of experiments on alcoholic fermentation, the authors have deduced the following results :—(1.) Slow fermentation at a low temperature reduces the formation of glycerol. In one case the fermentation lasted 25 days at 15°, when the proportion of alcohol to glycerol was 100 : 1·638. (2.) The minimum relation of 100 parts of alcohol to 7 parts of glycerol in the case of the fermentation of the juice of the grape, is not at all applicable to a solution of pure sugar. The average ratio in 21 fermentations of pure sugar solutions with ordinary beer yeast was 100 : 4·6. (3.) The addition to sugar solutions of other food, results in the formation of a high proportion of glycerol. (4.) The presence or absence of air during fermentation appears to have no influence on the result. (5.) A temperature of 35° reduces the rate of fermentation, and at the same time the proportion of glycerol is diminished. The rate of fermentation may be reduced by using a concentrated solution of sugar, but in this case the proportion of glycerol is increased. J. W. L.

Combination of Mannitol with Aldehydes of the Acetic Series. By J. Meunier (*Compt. rend.*, **108**, 408—410).—If aldehyde vapour is passed into a solution of mannitol in sulphuric or hydrochloric acid, the aldehyde is absorbed. The same reaction takes place if similar solutions of mannitol are agitated with paraldehyde, and the liquid becomes semisolid, owing to the separation of small, white, silky needles.

The product is the same in both cases, and forms slender, white needles which melt at 174° if rapidly heated, but sublime at a much lower temperature if gradually heated. Sublimation is rapid at 100—110°, and the product condenses in long, flexible needles. It is insoluble in cold water, but dissolves in 100 parts of water at 95°, it is only slightly soluble in cold alcohol, but dissolves readily in boiling alcohol. When it is suspended in water containing 2 per cent. of sulphuric acid and steam is passed into the liquid, the compound is decomposed into mannitol and aldehyde. When heated with water containing a higher proportion of acid, it decomposes below 100° into mannitol and other products which have not yet been investigated. The quantity of mannitol is greater the lower the temperature at which decomposition takes place, and the smaller the proportion of acid present.

This compound is an acetal formed by the union of mannitol with paraldehyde with elimination of 3 mols. H_2O. When the acetal is formed from gaseous aldehyde, the conditions are identical with those under which aldehyde changes into paraldehyde.

When an acid solution of mannitol is agitated with a mixture of acetaldehyde and benzaldehyde in equal proportions, the ethyl compound is formed first. C. H. B.

Sorbite and its Occurrence in the Fruits of Rosaceæ. By C. Vincent and Delachanal (*Compt. rend.*, **108**, 354—356).—The sorbite was separated in the form of the dibenzoic acetal from concentrated solutions which had previously been fermented with beer yeast, and treated with basic lead acetate. Unlike mannitol (preceding Abstract), it yields no acetal with the aldehydes of the acetic series. Sorbite was obtained from pears, apples, medlars, the fruit of the evergreen thorn, and Brittany cider. With a Laurent's shadow polarimeter and a tube 50 cm. long, it was found that the rotatory power is $[\alpha]_D = -1°73'$, so that sorbite, like mannitol, is lævogyrate, and contains asymmetrical carbon-atoms. The rotatory power is increased, but its direction is changed by the addition of sodium borate. In a liquid which contains in 100 c.c. 40 grams of crystallised borax, 30 grams of sodium hydroxide solution of 36°, and 10 grams of sorbite, the rotatory power of the latter at 15° is $[\alpha]_D = +12° 33'$.

When a dilute solution of sorbite is oxidised in the cold with a limited quantity of potassium permanganate, it yields a reducing sugar and an acid. If the product is warmed with potassium hydroxide solution, an intense yellow coloration is produced. The oxidised solution reduces ammoniacal silver nitrate and Fehling's solution energetically even in the cold.

If 1 part of sorbite is added to 2 parts of fuming nitric acid, or to a mixture of 4 parts of nitric acid and 10 parts of sulphuric acid, no nitrogen oxides are evolved, but an oil separates and rises to the top. The product is poured into a large quantity of water, the oil separated by treatment with ether, the ethereal solution agitated first with a solution of potassium carbonate, then with the solid salt and the ether expelled by slow evaporation. The yellow oil thus obtained is a nitro-derivative, which takes fire in contact with a burning substance and detonates violently when struck with a hammer.

C. H. B.

Quercitol. By H. KILIANI and C. SCHEIBLER (*Ber.*, **22**, 517—520).—When finely divided quercitol (5 grams) is treated with nitric acid of sp. gr. 1·39 (15 grams) first at 20° for about 12 hours and then at about 30° until evolution of gas ceases, mucic acid (5 to 6 per cent.) separates from the solution in the form of a colourless, crystalline powder. The colourless mother-liquors on neutralisation with calcium carbonate gradually become deep-red, and on mixing the filtered solution with alcohol, impure calcium trihydroxyglutarate is precipitated. This acid, which is only formed in very small quantities, was identified by means of the normal calcium salt (this vol., p. 32).

These results seem to show that Kanonnikoff's constitutional formula for quercitol is not correct. F. S. K.

Saccharification of Dextrin by Diastase. By L. LINDET (*Compt. rend.*, **108**, 453—455).—The author has reinvestigated the influence of maltose in checking the conversion of dextrin into sugar by the action of diastase. Phenylhydrazine was used to completely or partially remove maltose from the liquid. In an ordinary wort or must, saccharification stops when the maltose reaches a maximum, but recommences if the maltose is removed by alcoholic fermentation or by precipitation. These results confirm the earlier experiments of Payen. C. H. B.

Formation of Saccharoses from Formaldehyde. By O. LOEW (*Ber.*, **22**, 470—478).—As has been previously stated (compare Abstr., 1888, 358), some bases have the power of causing the condensation of formaldehyde to a far greater extent than others; lead oxide, for example, although without action in the cold, has a remarkably powerful action at a moderately high temperature even when present in very small quantities. Lime is a better agent than baryta, and both are far more powerful than soda or potash. A 3 per cent. solution of formaldehyde was shaken with a little lime; after half an hour the solution was filtered and divided into two portions, to one of which concentrated sodium carbonate solution was added as long as a precipitate of calcium carbonate was produced. After keeping for four days in closed vessels, condensation was at an end in the portion containing lime, but in the solution containing soda not a trace of sugar was formed, even after six days, the aldehyde having been partially converted into formic acid, but the greater part remaining unchanged. On warming this solution, a small quantity of sugar was formed, but it was immediately decomposed again, the solution becoming yellow. In other experiments with potash and soda, 1 per cent. of the alkali was added to a 1 per cent. solution of formaldehyde and kept at the ordinary temperature; the results were as unsatisfactory as before. When a 0·1 per cent. solution of formaldehyde is gently warmed with a 0·1 per cent. solution of potassium carbonate for several hours, a product similar to crude formose is obtained. As a rule the more concentrated the formaldehyde solution and the stronger the base, the larger the quantity of formic acid produced and consequently the smaller the quantity of sugar. Magnesia produces no condensation in a 1 per cent. or even in a 0·1 per cent. solution of formaldehyde, even on heating at 80—90° for several days; the solution obtained by shaking lead oxide with magnesium sulphate (*loc. cit.*) contains a small quantity of lead oxide, and it is to this base alone that condensation is due. The production of sugar which is observed when dilute formaldehyde solutions are treated with metallic lead is also due to the formation of lead oxide or hydroxide. When a solution of formaldehyde is heated at 80—90° with granulated metallic lead, slight evolution of gas occurs, and the solution becomes turbid owing to the separation of lead hydroxide; only traces of sugar are formed during the first hour, but at the end of the third hour condensation is complete. In presence of sulphates, the lead is attacked much more slowly, no turbidity is produced, and the condensation takes 6 to 10 times as long. The condensing action of commercial tin (*loc. cit.*) is due to the presence of small quantities of lead, and the sugar (pseudo-formose) which is formed is a mixture of several isomeric saccharoses.

The condensing action of bases is doubtless due to the intermediate formation of some unstable compound of formaldehyde with the base, as is shown by the fact that a solution of formaldehyde, free from formic acid, dissolves more lime than water does.

When litharge (about 15 grams) is warmed with a 16—20 per cent. solution of formaldehyde (25 c.c.), the oxide increases considerably in volume and becomes converted into a white, spongy mass, a small portion being reduced to metal. This powder, after washing with water, pressing, and drying over sulphuric acid, contains unchanged lead oxide, probably also hydroxide, but on heating, it blackens with separation of metallic lead and is then immediately converted into the yellow oxide. It has no smell, but when heated alone, or with water, or with dilute sulphuric acid, the penetrating odour of formaldehyde is perceptible. It reduces silver nitrate solution at the ordinary temperature, the metal being deposited. This white powder is, therefore, a compound of lead oxide and formaldehyde, and its formation is distinct evidence in favour of the glycol formula for the latter.

Numerous experiments were made under varying conditions with bases, compounds of bases (amongst others calcium and magnesium acetate), and salts with an alkaline reaction, but no naturally occurring saccharose was obtained. A feeble electric current passed through the mixture was also without effect on the result. It was noticed, however, that seemingly inconsiderable alterations in the mode of condensation often influenced the relative quantities of the various sugars produced, and it was found that by diminishing the quantity of the condensing agent the proportion of the more stable sugars could be augmented. Formose, on the other hand, is formed when condensation takes place easily and rapidly.

The author gives hypothetical graphic formulæ for formose and levulose, and also attempts to show by graphic formulæ in what manner the condensation of formaldehyde by lime may be supposed to take place. According to these views a base containing more than two hydroxyl-groups would limit the freedom of rotation of the carbon-atoms, and would lead to an increased formation of those sugars analogous to the natural saccharoses. The striking energy of lead oxide may, therefore, be due to the existence of a hydrate, $Pb_2(OH)_4$, and with this base the author succeeded in obtaining a mixture of sugars, amongst which is one (*methose*) which ferments with yeast. The method which yields the largest proportion of this sugar (about 20 per cent.) was found to be the following:—Formaldehyde (40 grams) in aqueous solution of known strength is added to water (4 litres), the solution mixed with magnesia (0·5 gram) and magnesium sulphate (2 to 3 grams), and then warmed at about 60° with granulated lead (350—360 grams) in a flask, which the solution fills almost entirely. The reaction is at an end when a small portion, on boiling, no longer smells of formaldehyde, which is the case after about 12 hours. The almost colourless syrup which remains when the solution is evaporated at 50°, is boiled with 80 per cent. alcohol, the cold solution mixed with ether to precipitate magnesium sulphate, and most of the sugar then precipitated by adding ether and light petroleum. The product is again dissolved in absolute alcohol, the solution mixed with ether, the precipitated syrup dissolved in water, and the alcohol driven off by evaporation. The yellowish, extremely sweet syrup which is thus obtained reduces Fehling's solution very energetically, and is less readily attacked by bromine than is dextrose; it yields humous substances when warmed with hydrochloric acid, gives a yellowish-brown colour with alkalis, and shows all the most important properties of a natural saccharose. It enters into lively fermentation when treated with yeast in aqueous solution, but a large quantity of the sugar, probably formose, remains unchanged even when left in contact with yeast for eight days; the ethyl alcohol produced was identified by its smell, by the iodoform reaction, and by oxidation to acetaldehyde. The crude syrup is almost completely decomposed when warmed for three hours with 7·5 per cent. hydrochloric acid, yielding humous substances and furfuraldehyde, so that the sugar which ferments resembles levulose rather than dextrose. (Compare Sieber, *Zeit. anal. Chem.*, **24**, 137.) The crude syrup yields an oily mixture of osazones from which, by washing with cold 96 per cent. alcohol and recrystallising the residue, an osazone, $C_{18}H_{22}N_4O_5$, melting at 205—206°, can be isolated. This compound crystallises in yellow needles, and in appearance and solubility in absolute alcohol is very similar to phenylglucosazone. That this osazone is a derivative of the fermenting sugar is shown by the following experiments:—Two equal portions (10 c.c.) of the crude syrup were taken; one was mixed with 8 vols. of water and fermented with yeast for one day at the ordinary temperature. The osazones were then prepared from the two portions separately, and treated in the same way with benzene, ether, and cold absolute alcohol. The weight of the residual sparingly soluble osazone obtained from the non-fermented portion was 26 per cent. of the total mixture of osazones, in the other case it only amounted to 11·5 per cent. The osazone (0·4 gram) was reconverted into sugar by Fischer's method (*Ber.*, **22**, 87); the sugar fermented with yeast, but only slowly, and was not entirely decomposed until the third day, perhaps owing to the diluteness of the solution. F. S. K.

Formose. By O. Loew (*Ber.*, **22**, 478—482).—The mixture of osazones which is obtained from the crude formose, prepared by treating a 3·5—4 per cent. solution of formaldehyde with lime, consists principally of three compounds (compare Fischer, Abstr., 1888, 590):—(1) Formosazone, which constitutes 75—82 per cent., or probably more, of the crude product; this compound is readily soluble in ether, and thereby differs from all other known osazones; (2) an osazone (16—20 per cent.), probably a mixture, which is sparingly soluble in ether, but very readily soluble in absolute alcohol; (3) an osazone (3—4 per cent.) insoluble in ether and very sparingly soluble in cold, absolute alcohol. The relative quantity of formose in the crude product is considerably diminished when more dilute solutions of formaldehyde are employed, and when a large quantity of thin milk of lime is used instead of a thick paste; with a 1 per cent. solution the formosazone only forms 48—53 per cent. of the total osazone weight.

Pure formose, prepared from the osazone, is a syrupy sugar, readily soluble in strong alcohol and very easily changed by acids or alkalis. When warmed with hydrochloric acid it yields humous substances, but no levulose, and when heated at about 100° it turns brown, and is converted into a substance with a bitter taste. It undergoes the lactic fermentation, but does not ferment with yeast. Bromine acts on it more rapidly than on levulose, but much more slowly than on dextrose, converting it into oxalic acid and another acid, probably trihydroxybutyric acid; it is also oxidised by nitric acid, but no acid containing six atoms of carbon is produced. Its reducing power for Fehling's solution is about the same as that of dextrose, but when treated with nascent hydrogen it is converted into a syrupy substance which has no reducing action. It combines readily with hydrocyanic acid, but the product is easily decomposed by concentrated mineral acids. The osazone (see above) begins to melt at about 130°.

The article concludes with a reply to Fischer (*loc. cit.*) in which the author claims that he himself, and not Butlerow, first showed that several saccharoses could be obtained from formaldehyde.

F. S. K.

Conversion of Ketones into Nitrosoketones. By L. Claisen and O. Manasse (*Ber.*, **22**, 526—530).—Nitrosoketones can be obtained, as has been previously shown (Abstr., 1887, 944), by treating ketones with amyl nitrite in presence of sodium ethoxide or hydrochloric acid. Further investigations have shown that with some ketones sodium ethoxide, with others hydrochloric acid, gives the best results. Diethyl ketone and benzalacetone belong to the second category, nitrosomesityl oxide, on the other hand, can only be obtained by using sodium ethoxide. The nitroso-derivative of methyl propyl ketone and phenyl ethyl ketone can be prepared by either method, but the yield is better when hydrochloric acid is employed.

In preparing nitrosoketones by means of amyl nitrite and hydrochloric acid, it is best to proceed as follows:—A small quantity of amyl nitrite is added to the ketone, then a little hydrochloric acid, and as soon as, but not before, the yellow coloration has disappeared, the calculated quantity of amyl nitrite is gradually added in small portions to the well-cooled mixture, care being taken that the yellow colour has disappeared before each fresh addition of the nitrite. After keeping for a short time, the product is extracted with dilute soda, the alkaline solution shaken with ether to remove amyl alcohol, acidified with acetic acid or dilute hydrochloric acid, and the nitrosoketone extracted with ether. In the case of benzalacetone and propiophenone, it is not necessary to extract with soda, as the product can be precipitated at once, and almost entirely by adding excess of light petroleum. The yield varies considerably, being in many cases 30—40 per cent., in others as much as 70 per cent. of the calculated quantity. Excess of amyl nitrite should never be present during the reaction, as the nitrosoketones are thereby readily decomposed. Nitrosoethyl phenyl ketone (*loc. cit.*) is decomposed by amyl nitrite, yielding benzoyl acetyl, amyl alcohol, and nitrous oxide; nitrosoacetone and nitrosoacetophenone are decomposed when warmed with amyl nitrite, but the reaction seems to take place in a different manner.

Propyl nitrosomethyl ketone, $COPr\cdot CH\colon NOH$, crystallises from light petroleum in small, nacreous plates, melting at 48—51°. The *osazone*, $N_2HPh\colon CH\cdot CPr\colon N_2HPh$, crystallises in needles and melts at 162—163°. The *glyoxime*, $CPr(NOH)\cdot CH\colon NOH$, melts at 168°.

Nitrosodiethyl ketone, $OH\cdot N\colon CMe\cdot COEt$, crystallises in colourless plates melting at 59—62°. The *osazone*, $N_2HPh\colon CEt\cdot CMe\colon N_2HPh$, melts at 166—169°. The *glyoxime* is a crystalline powder melting at 170—172°.

These two nitrosoketones are isomeric with methyl nitrosopropyl ketone, prepared by Meyer and Züblin (Abstr., 1878, 659) from ethyl ethylacetoacetate.

Nitrosomesityl oxide, $CMe_2\colon CH\cdot CO\cdot CH\colon NOH$, crystallises from benzene and light petroleum in colourless prisms melting at 102°.

Nitrosopropiophenone, $COPh\cdot CMe\colon NOH$, crystallises from alcohol and water in small, colourless needles melting at 108—110°.

Nitrosobenzalacetone, $CHPh\colon CH\cdot CO\cdot CH\colon NOH$, can be prepared as described above, or by gradually adding a mixture of nitrosoacetone, benzaldehyde, and ether, to well-cooled ether containing sodium ethoxide in suspension, and decomposing the ice-cold solution of the resulting sodium salt with acids. It crystallises well from water, benzene, ethyl acetate, and chloroform, melts at 143—144°, and gradually decomposes with evolution of hydrogen cyanide.

F. S. K.

Decomposition of Fats by Heating under Pressure. By C. Engler (*Ber.*, **22**, 592—597; compare Abstr., 1888, 928).—Two series of experiments with fish oil and oleïc acid showed that when such compounds are distilled under increased pressure, the quantity of methane produced is increased and the quantity of carbonic anhydride diminished.

When fish oil is heated under the ordinary atmospheric pressure, the greater portion distils between 360° and 420°, but in the closed glass vessels previously described (*loc. cit.*) it passes between 365° and about 425°. In the latter case, the principal portion (63·1 per cent.) distils in the form of liquid hydrocarbons (sp. gr. 0·837), and considerable quantities (8·9 per cent.) of gaseous products, such as methane, olefines, carbonic oxide, and carbonic anhydride, are formed; the residual tarry mass, when heated under the ordinary atmospheric pressure, yields liquid hydrocarbons (16·5 per cent.) and coke or asphalte (11·6 per cent.). Trioleïn, when treated in like manner, yields liquid hydrocarbons (69·8 per cent., sp. gr. 0·845) and gaseous products (10 per cent.); the residue, on further distillation under the ordinary pressure, yields liquid hydrocarbons (14·1 per cent.) and coke or asphalte (6·1 per cent.). If the small quantity of water which is formed and the undecomposed oil or trioleïn in the distillate is taken into account, the yield of crude oily hydrocarbons is 69·5 per cent. in the case of fish oil, and 73·7 per cent. in case of trioleïn; the conversion into paraffins is almost complete with one distillation. The following paraffins were isolated from the distillate of fish oil:—Secondary hexane (diisopropyl), boiling at 57—59°; sp. gr. 0·6677 at 21°. Secondary heptane (ethylisoamyl), boiling at 88—91°, sp. gr. 0·6918 at 18°. Normal octane, boiling at 123—125°; sp. gr. 0·7044 at 19°. Secondary octane (diisobutyl), boiling at 107—109°; sp. gr. 0·702 at 17·5°. Normal nonane, boiling at 148—151°; sp. gr. 0·729 at 20·5°.

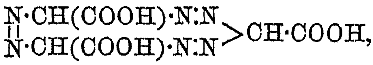
The fraction 140° to 300° of the crude distillate obtained from fish oil, after purifying, burns in an ordinary petroleum lamp with a highly luminous flame.

The crude product, which is obtained when trioleïn is distilled under pressure (10 atmos.), is a mobile, brownish-black, fluorescent oil of sp. gr. 0·780, and very similar to that obtained from fish oil. It contains 2·5 per cent. of ethereal salts, and yields to water 1·6 per cent., to soda 2 per cent., to concentrated sulphuric acid 15 per cent., and to fuming sulphuric acid 10 per cent. of its weight. From the residue, normal hexame and normal heptane were isolated.

F. S. K.

Constitution of Diazo- and Azo-compounds of the Fatty Series, and of Hydrazine (Diamide) and its Derivatives. By T. Curtius (*J. pr. Chem.* [2], **39**, 107—139).—The author discusses these questions in the light of his recent researches on the subject (this vol., pp. 340, 369, 376, 393). The constitution of ethyldiazoacetate is $\overset{N}{\underset{N}{\|}}>CH\cdot COOEt$, containing the group $\left(\overset{N}{\underset{N}{\|}}>C\right)''$, which characterises the diazo-compounds of the fatty series.

Triazoacetic acid has the constitution

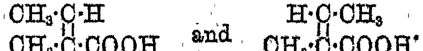


$$\left.\begin{array}{l} N\cdot CH(COOH)\cdot N{:}N \\ \| \\ N\cdot CH(COOH)\cdot N{:}N \end{array}\right> CH\cdot COOH,$$

which explains its splitting up under the action of water into hydrazine, $H_2N\cdot NH_2$, and oxalic acid (or formic acid and carbonic anhydride).

Hydrazine hydrate is $H_2N\cdot NH_3\cdot OH$; it evaporates completely in a vacuum over caustic potash, and solidifies in a mixture of solid carbonic anhydride and ether to a crystalline mass, which melts below —40°. A. G. B.

Bromine Additive Products of Angelic and Tiglic Acids. By M. Pückert (*Annalen*, **250**, 240—250).—Angelic acid is best prepared by shaking a mixture of oil of Roman camomile (100 grams) with potassium hydroxide (51 grams) and water (51 grams), until the whole solidifies. After a few days a small quantity of water is added, and the layer of alcohol which rises to the surface is removed. The aqueous solution is acidified with sulphuric acid and extracted with ether. The residue which remains after evaporating the ethereal solution is pressed between bibulous paper and distilled. It melts at 45—46°, and boils at 185°. 100 grams of oil of camomile yield 15 grams of angelic acid. Tiglic acid can be most economically prepared by slowly adding 150 grams of 2 per cent. sodium amalgam to 10 grams of ethyl methylacetoacetate dissolved in 30 grams of water and a sufficient quantity of alcohol to yield a clear solution; during the operation, sulphuric acid is added so as to keep the mixture slightly acid, and from time to time the liquid mercury must be run off, and crystals of sodium sulphate removed. When all the amalgam is added, the solution is neutralised, evaporated to dryness, and extracted with absolute alcohol. The alcoholic solution is evaporated, the residue acidified with sulphuric acid and extracted with ether; the ethereal extract is evaporated, and the residue on distillation yields tiglic acid. The dibromides are formed by slowly adding bromine diluted with carbon bisulphide to a solution of the acids in carbon bisulphide. *Tiglic dibromide* melts at 86—87°, and is insoluble in cold water, in which it remains in the crystalline state. *Angelic acid dibromide* melts between 50° and 57°, but after fusion it melts constantly at 64°. It is hygroscopic and liquefies in water. Tiglic acid dibromide is decomposed by sodium carbonate, yielding crotonylene hydrobromide. Under similar conditions angelic dibromide yields monobromopseudobutylene. The crotonylene hydrobromide is more easily reduced by an alcoholic solution of sodium ethoxide than the isobromopseudobutylene from angelic dibromide. These results indicate that angelic and tiglic acids are geometric isomerides, having respectively the constitutions represented by the following formulæ:—



$$\begin{array}{l} CH_3\cdot C\cdot H \\ \quad\ \ \| \\ CH_3\cdot C\cdot COOH \end{array} \text{ and } \begin{array}{l} H\cdot C\cdot CH_3 \\ \quad\ \| \\ CH_3\cdot C\cdot COOH \end{array}$$

W. C. W.

Ethyl Monochloracetoacetates. By A. HALLER and A. HELD (*Compt. rend.*, **108**, 516—518).—Ethyl γ-monochloracetoacetate was obtained by the direct action of chlorine on the acetoacetate at a low temperature. On fractionation, the chlorine-derivative boiled at 188—189°. A solution of the monochloracetoacetate in anhydrous ether or benzene was allowed to act on half its weight of pure potassium cyanide, the product was filtered, the filtrate treated with a further quantity of the cyanide, and the process repeated a second time. The formation of a certain quantity of insoluble ethyl acetocyanacetate showed that some α-monochloracetoacetate was present. The ether was expelled from the filtrate and the residue was fractionated; unaltered chloracetoacetate passed over, and the remaining cyanogen-derivative boiled at 145—160° in a vacuum. The latter was treated with an alcoholic solution of hydrogen chloride, the precipitate of ammonium chloride separated, and the ethereal salt treated with hydrocyanic acid, and afterwards with an alcoholic solution of hydrogen chloride. After removal of ammonium chloride and ether and distillation in a vacuum, a small quantity of liquid was obtained which boiled at 200°, and when saponified yielded a solution which with lime-water gave the reaction for citric acid.

C. H. B.

Syntheses by means of Ethyl Cyanosuccinate. By L. BARTHE (*Compt. rend.*, **108**, 297—300).—The hydrogen of the CH group in ethyl cyanosuccinate is readily displaced by metals or by alkyl radicles. The substitution of metals is effected by treatment with alkyl-metallic oxides; the substitution of alkyl radicles is accomplished by mixing the ethyl cyanosuccinate with a solution of an equivalent quantity of sodium in the particular alcohol and boiling the mixture with the corresponding alkyl iodide. The excess of alcohol is distilled off, the residue diluted with water, extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The products are colourless, oily liquids, of the general formula

$$COOEt{\cdot}CH_2{\cdot}CR(CN){\cdot}COOEt.$$

Ethyl methylcyanosuccinate boils at 183—186° under a pressure of 3·5 mm.; *ethyl ethylcyanosuccinate* boils at 170—180° in a vacuum; *ethyl propylcyanosuccinate* boils at 204—206° under a pressure of 45 mm.

If ethyl ethylcyanosuccinate is allowed to remain for several weeks in contact with alcohol saturated with hydrogen chloride, it yields *ethyl ethylethenyltricarboxylate*, $COOEt{\cdot}CH_2{\cdot}CEt(COOEt)_2$; this boils at 187° under a pressure of 50 mm. C. H. B.

Action of Bromine on Aconitic and Carballylic Acids. By E. GUINOCHET (*Compt. rend.*, **108**, 300—302).—Aconitic acid, when heated in sealed tubes at 115—120° for several hours with four molecular proportions of bromine, yields tribromocarballylic acid, $C_6H_5Br_3O_6$, which separates from alcohol of 90° in colourless crystals, very soluble in ethyl alcohol, methyl alcohol, ether, and acetone, but insoluble in cold water and in chloroform. It decomposes slowly at 100°, and dissolves rapidly in hot water with decomposition and liberation of hydrogen bromide. When boiled with barium hydroxide, it yields a considerable proportion of oxalic acid. The potassium salt of tribromocarballylic acid forms a crystalline powder containing 1·5 mols. H_2O; the ammonium salt crystallises in prisms very soluble in water; and the barium salt crystallises with 12 mols. H_2O in colourless prisms which are very soluble in water, but do not dissolve in ethyl alcohol. The barium salt loses 9 mols. H_2O in a dry vacuum or when exposed to air, and then undergoes no change at 100°, but begins to decompose at 115°. Cold aqueous solutions of all these salts give no precipitate with silver nitrate, but a hot solution gives an immediate precipitate of silver bromide.

The action of bromine on carballylic acid yields the same derivative. In the first case, the tribromocarballylic acid is formed from the aconitic acid by direct addition of two atoms of bromine and substitution of one atom of bromine for an atom of hydrogen, the change being analogous to the formation of carballylic acid by direct union of aconitic acid with two atoms of hydrogen. C. H. B.

Oxidation of Galactosecarboxylic Acid. By H. Kiliani (*Ber.*, **22**, 521—524).—Galactosecarboxylic acid (Abstr., 1888, 581) is best prepared in large quantities by boiling the crude product of the action of hydrocyanic acid on galactose with lime; the lime is precipitated in the cold with oxalic acid, the filtered solution boiled with lead carbonate and concentrated, crystallisation being promoted by rubbing with a small quantity of the crystalline lead salt. The latter is obtained from a small quantity of the pure acid, which is prepared by the method previously described (*loc. cit.*). The crystals are separated after one to two days, and purified by crystallising twice from boiling water (4 parts) with addition of animal charcoal. The pure salt is dissolved in water (5 parts), treated with hydrogen sulphide, and the filtered solution evaporated under diminished pressure to avoid the formation of the lactone.

Carboxygalactonic acid, $C_7H_{12}O_9$, is formed when galactosecarboxylic acid (1 part) is heated at 50° for about 24 hours with nitric acid of sp. gr. 1·2 (1½ parts). The solution is evaporated until free from nitric acid, taken up with water, the oxalic acid precipitated with the requisite quantity of calcium carbonate, and the filtered solution neutralised with potash, evaporated to a syrup, and mixed with a large excess of acetic acid. *Potassium hydrogen carboxygalactonate*, $2C_7H_{11}O_9K + 3H_2O$, separates on stirring, the whole becoming solid after 12 to 24 hours. It is purified by recrystallisation from water, from which it separates in aggregates of silky needles; it readily forms supersaturated solutions, from which it can be separated by adding alcohol or stirring. The *cadmium* salt, $C_7H_{10}O_9Cd,2H_2O$, prepared by decomposing a solution of the neutral potassium salt with cadmium nitrate, crystallises in colourless, nodular masses, consisting of small, slender needles. The free *acid* is obtained in microscopic prisms when a solution of the cadmium salt is treated with hydrogen sulphide, filtered and evaporated in a partial vacuum. It sinters together at 168°, melts at 171° with decomposition, and is sparingly soluble in cold water, although more readily than mucic acid. The neutral potassium and sodium salt could not be obtained in crystals. The *barium* salt, $(C_7H_{10}O_9)_2Ba + 3H_2O$, crystallises in small prisms or needles. F. S. K.

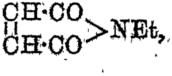
Metasaccharic Acid. By H. Kiliani (*Ber.*, **22**, 524—525).—Maquenne (Abstr., 1888, 677) has observed that the diphenylhydrazide of ordinary saccharic acid has the same melting point as that of metasaccharic acid, and resembles the latter in being almost insoluble in water, alcohol, and ether. The author finds by direct comparison that these two compounds can hardly be distinguished one from the other.

The diacetyl-derivative of the double lactone of metasaccharic acid can be prepared by treating the anhydrous double lactone (2 grams) with acetic anhydride (3 grams) and concentrated sulphuric acid (3 drops). It melts at 155°, and is readily soluble in hot, glacial acetic acid, from which it crystallises in well-defined prisms. This compound is therefore quite different from the corresponding derivative of saccharic acid (compare Maquenne, *loc. cit.*), which crystallises in small rhombic plates melting at 188°. F. S. K.

Preparation of Glycocine. By S. Gabriel and K. Kroseberg (*Ber.*, **22**, 426—428).—Glycocine is best prepared by heating potassium phthalimide (100 grams) with ethyl chloracetate (65 grams) at 140—150° (compare Goedeckemeyer, Abstr., 1888, 1294). The product is poured into a dish, the powdered cake recrystallised from boiling 50 per cent. alcohol, and washed first with dilute alcohol and then with water. The yield of ethyl phthalylglycollate is about 97 per cent. of the theoretical quantity. This compound is then decomposed by heating with concentrated hydrochloric acid at 200° (compare Goedeckemeyer, *loc. cit.*), when it yields about 96 per cent. of the theoretical quantity of glycocine hydrochloride.

In preparing glycocine in large quantities, the phthalyl-derivative (1 mol.) is hydrolysed by boiling for a short time with alcoholic potash (10 per cent., 2 mols.). The clear liquid is mixed with fuming hydrochloric acid (2 mols.) and the glycocinephthaloylic acid, which crystallises from the cold solution, is separated and washed with ice-cold water. The yield is about 85·5 per cent. of the theoretical quantity. The acid is then boiled for about two hours with twice its weight of pure hydrochloric acid (20 per cent.) with constant shaking, and the diluted solution is separated from the phthalic acid by filtration and evaporated. The residue is extracted with a small quantity of ice-cold water, the extract evaporated, and the residual glycocine hydrochloride washed with absolute alcohol.

Glycocinephthaloylic acid, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot COOH$, softens at about 100° and melts at 105—106° (compare Beese, Abstr., 1888, 148). F. S. K.

Ethylfumarimide. By A. Piutti (*Chem. Centr.*, 1888, 1529).—If ethylamine hydrogen malonate is heated at 160—200°, water and an oil distil over. The latter, *ethylfumarimide*,  $\begin{matrix}CH\cdot CO\\ \| \\ CH\cdot CO\end{matrix}\!\!>\!NEt$, solidifies in crystals, is volatile and caustic, and the vapours cause a flow of tears. It is little soluble in water, very soluble in alcohol and ether, considerably soluble in benzene; from the latter it may be obtained in thick, lustrous crystals. It forms two compounds with bromine in ethereal solution, a liquid and a solid derivative; the latter is little soluble in ether, and does not melt at a high temperature. When heated with zinc-dust, ethylfumarimide emits vapours which, when brought into contact with a splinter of pinewood moistened with hydrochloric acid, give the pyrroline reaction. When reduced with sodium amalgam, an oil is formed. With aqueous or alcoholic alkali solutions, a beautiful purple colour is obtained; by heating with solid potassium hydroxide, a violet substance is formed, which evolves ethylamine at a higher temperature. From the aqueous solution of the fused mass, hydrochloric acid precipitates fumaric acid. If ethylfumarimide is dissolved in somewhat concentrated potassium hydroxide solution, *potassium ethylfumaramate* is formed; the free acid may be obtained from this on the addition of a mineral acid.

Ethylfumaramic acid, $NHEt·CO·CH{:}CH·COOH$, melts at 125—126°, crystallises in lustrous, pearly scales, is very readily soluble in hot water and alcohol, fairly soluble in ether, insoluble in benzene. When heated, ethylfumarimide is regenerated. It combines directly with bromine. The copper salt is a blue, amorphous precipitate; the silver salt crystallises from water in microscopic needles.

J. W. L.

Substituted Asparagines. By A. PIUTTI (*Chem. Centr.*, 1888, 1530—1531).—*β-Ethylasparagine*, $NH·Et·CO·CH_2·CH(NH_2)·COOH$, is prepared by the action of a solution of ethylamine in alcohol on ethyl β-aspartate. An ethylamine salt first crystallises out, which melts at about 255° with decomposition. It reacts with cupric acetate to form the copper salt of β-ethylasparagine, which crystallises out in light-blue, pearly flakes, nearly insoluble in water. Hydrogen sulphide decomposes this, and the precipitated β-ethylasparagine is purified by recrystallisation from water. It forms thin, lustrous flakes melting at 258—260° with decomposition. It is not decomposed by magnesia, but with 30 per cent. potassium hydroxide it yields ethylamine and inactive aspartic acid. β-Ethylasparagine is optically inactive.

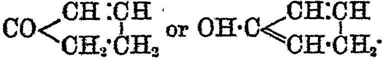
β-Allylasparagine, $C_3H_5·NH·CO·CH_2·CH(NH_2)·COOH$, is prepared in an exactly similar manner to the foregoing. It crystallises from water in lustrous, pearly flakes, melting at 258° with decomposition. It is anhydrous, readily soluble in hot water, but little soluble in cold water, and very sparingly soluble in alcohol and ether. It is optically inactive.

J. W. L.

Attempts to prepare Titanium Ethyl. By E. PATERNÒ and A. PERATONER (*Ber.*, 22, 467—470). The compound $TiCl_4,2ZnEt_2$ is obtained when titanium chloride (1 mol.) is gradually added to well-cooled zinc ethyl (2 mols.). An energetic reaction occurs, but no gas is evolved, and as soon as all the chloride has been added the whole solidifies to a brown mass which is not changed even on heating. It is decomposed with violence when mixed with water, yielding metallic zinc and a small quantity of an oil which can be separated by distilling with steam. This oil has no constant boiling point, but it can be separated into two fractions, namely, a portion boiling at 120—130°, which was proved to be octane, and a portion boiling at 220—270°, which contains considerable quantities (7·72 per cent.) of titanium, and is probably a mixture of octane and titanium ethyl.

F. S. K.

Condensation of β-Ketonic Ethers with Bibasic Acids. By R. Fittig (*Annalen*, **250**, 166—178).—A discussion of the constitution of the condensation products of succinic and pyruvic acids with ethyl acetacetate and ethyl benzoylacetate, described in the following Abstracts. All these compounds are derived from the compound

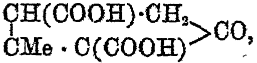


$CO<\begin{matrix}CH:CH\\ CH_2\cdot CH_2\end{matrix}$ or $OH\cdot C<\begin{matrix}CH:CH\\ CH\cdot CH_2\end{matrix}$.

W. C. W.

Condensation of Ethyl Acetoacetate and Succinic Acid. By F. v. Eynern (*Annalen*, **250**, 178—192).—*Ethyl hydrogen methronate*, $C_8H_7O_5Et$, is prepared by heating for 10 hours a mixture in molecular proportions of ethyl acetoacetate, acetic anhydride, and powdered sodium succinate which has been dried at 150°; the product is dissolved in water and extracted with ether. The liquid which is left on evaporating the ethereal extract is rendered alkaline with sodium carbonate, and again treated with ether to remove any unaltered ethyl acetoacetate; the alkaline solution is acidified with hydrochloric acid, and the new acid dissolved out with ether. Ethyl hydrogen methronate crystallises in needles and melts at 75·5—76°; it is freely soluble in alcohol, ether, chloroform, and benzene. The calcium and barium salts crystallise in needles containing 2 mols. H_2O. The silver salt, $C_{10}H_{11}O_5Ag$, crystallises in needles and is soluble in hot water. Ethyl hydrogen methronate resembles ethyl hydrogen carbuvate in many respects. It is decomposed by boiling with baryta-water, yielding the barium salt of methronic acid.

Methronic acid,



$\begin{matrix}CH(COOH)\cdot CH_2\\ CMe\cdot C(COOH)\end{matrix}>CO$, melts at 204—205°, decomposes at a higher temperature, forming uvitic acid and carbonic anhydride, and dissolves in alcohol, benzene, and in hot water. The acid calcium salt, $(C_8H_7O_5)_2Ca$, is very sparingly soluble in water. The acid barium salt is much more freely soluble. The normal barium salt, $C_8H_6O_5Ba$, is amorphous. In analyses of silver methronate, the percentage of silver is invariably found too low for some unknown cause. *Diethylmethronate*, $C_8H_6O_5Et_2$, is prepared by saturating an alcoholic solution of ethyl hydrogen methronate with hydrogen chloride; it boils at 300—305°. Phenylhydrazine unites with ethyl hydrogen methronate, forming a crystalline compound of the composition $C_{16}H_{18}N_2O_4$; this melts at 133—134°, and is freely soluble in hot alcohol, but is insoluble in cold solutions of sodium carbonate or sodium hydroxide.

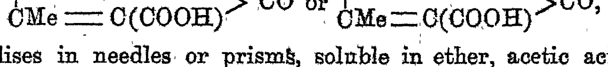
Phenylhydrazine and methronic acid unite together, forming a neutral compound of the composition $C_{14}H_{14}N_2O_4$; it melts at 211—212°

with decomposition, and is freely soluble in alcohol. Methronic acid is not attacked by nascent hydrogen. W. C. W.

Barium and Calcium Salts of Uvic, Carbuvic, and Ethylcarbuvic Acids. By P. Feist (*Annalen*, **250**, 192—195).—*Barium uvate*, $(C_7H_7O_3)_2Ba + 4H_2O$, crystallises in flat needles, soluble in hot water; the water of crystallisation is expelled at 120°. The *calcium* salt is deposited from a cold saturated solution in thick prisms containing 2 mols. H_2O, and from a hot solution in needles containing 4 mols. H_2O. *Carbuvic acid* is less soluble in water than methronic acid, but it is freely soluble in alcohol; it melts at 230°, and decomposes at a slightly higher temperature. *Barium carbuvate*, $C_8H_6O_5Ba + \frac{1}{2}H_2O$, is deposited as a crystalline precipitate when barium chloride is added to ammonium carbuvate. The calcium salt is anhydrous, and is less soluble than the barium salt. These salts do not resemble the salts of methronic acid. *Ethyl hydrogen carbuvate* is freely soluble in alcohol, chloroform, benzene, and in warm carbon bisulphide and in light petroleum. The barium salt, $(C_{10}H_{11}O_5)_2Ba + 4H_2O$, is soluble in hot water and crystallises in needles. The calcium salt, $(C_{10}H_{11}O_5)_2Ca + 3H_2O$, is also more soluble in hot than in cold water. These salts are quite distinct in their properties from those of ethyl hydrogen methronate. W. C. W.

Ethyl Acetoacetate and Pyruvic Acid. By A. Dietzel (*Annalen*, **250**, 195—211).—Ethyl hydrogen methylmethronate is formed by heating a mixture of equivalent quantities of ethyl acetoacetate, sodium pyruvate, and acetic anhydride in a large flask fitted with a reflux condenser. The temperature is gradually raised from 70° to 140°. The product is poured into a shallow basin and heated at 100°, with the occasional addition of small quantities of water in order to remove ethyl acetate, ethyl acetoacetate, and acetic acid; the residue is diluted with ether or chloroform and filtered, and after removing the ether or chloroform from the filtrate by evaporation, the residue is dissolved in boiling water and the solution energetically shaken. It is then treated with animal charcoal and extracted with ether. On evaporating the ether, ethyl hydrogen methylmethronate remains as a yellowish-red hygroscopic syrup. It is insoluble in water and carbon bisulphide, but is freely miscible with the usual solvents. It is decomposed by solutions of sodium hydroxide or baryta, forming the sodium or barium salt of methylmethronic acid. The acid is almost completely precipitated from these solutions by the addition of hydrochloric acid.

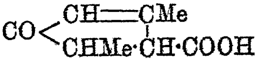
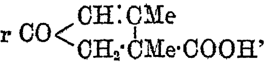
Pure *methylmethronic acid*,

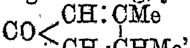


$$\left.\begin{array}{l}\mathrm{CH(COOH){\cdot}CHMe}\\ \mathrm{CMe{=\!=}C(COOH)}\end{array}\right>\mathrm{CO}\ \text{or}\ \left.\begin{array}{l}\mathrm{CMe(COOH){\cdot}CH_2}\\ \mathrm{CMe{=\!=}C(COOH)}\end{array}\right>\mathrm{CO},$$

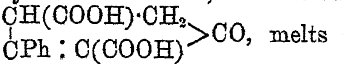
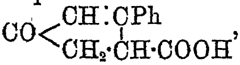
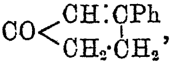
crystallises in needles or prisms, soluble in ether, acetic acid, hot alcohol, and in hot water. It melts at 198°. The barium salt, $C_9H_8O_5Ba + 2H_2O$, is deposited from its aqueous solution as a hygroscopic, amorphous mass, but it may be obtained in crystals by the cautious addition of alcohol to the aqueous solution. The calcium salt, $C_9H_8O_5Ca + 3H_2O$, resembles the barium salt in its properties. The silver salt, $C_9H_8O_3Ag_2$, is crystalline and sparingly soluble in hot water. No acid salts of methyl methronic acid are known.

Diethyl methylmethronate, $C_9H_8O_5Et_2$, boils with slight decomposition at 279—280° (uncorr.). It is insoluble in water, but miscible with other solvents. It is decomposed by boiling with an alcoholic solution of potassium hydroxide, yielding ethyl hydrogen methylmethronate, $C_9H_9O_5Et$, and by an aqueous solution of potassium carbonate, yielding potassium methylmethronate. The ethyl barium salt, $(C_{11}H_{13}O_5)_2Ba + H_2O$, is amorphous. The calcium salt, $(C_{11}H_{13}O_5)_2Ca + 2H_2O$, crystallises in needles which are soluble in water and in hot alcohol. The silver salt, $C_{11}H_{13}O_5Ag$, is freely soluble in alcohol and ether. The salts of the heavy metals are as a rule insoluble in water, and freely soluble in alcohol and ether.

Methyluvic acid,  $\mathrm{CO}<\begin{matrix}\mathrm{CH{=}CMe}\\ \mathrm{CHMe{\cdot}CH{\cdot}COOH}\end{matrix}$ or  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH_2{\cdot}CMe{\cdot}COOH}\end{matrix}$, is prepared by heating methylmethronic acid in an atmosphere of carbonic anhydride. It is less soluble in water than methylmethronic acid, but dissolves freely in alcohol, light petroleum, chloroform, benzene, ether, and acetic acid. The acid is reprecipitated from concentrated aqueous solutions by sulphuric acid, and from its alcoholic solution by hydrochloric acid. Methyluvic acid melts at 98° and sublimes at 100°, but melts under water at 85—86°. The barium salt, $(C_8H_9O_3)_2Ba + 4H_2O$, crystallises in rhombic prisms. The calcium salt also crystallises with 4 mols. H_2O in plates. It is insoluble in alcohol. The crystalline silver salt melts at 150°, decomposing into silver and methyluvic acid. The ethyl salt, $C_8H_9O_3Et$, boils at 218—219° (uncorr.), and is miscible with the usual solvents, excepting water; it is slowly decomposed by water, and rapidly by an alcoholic solution of potassium hydroxide, yielding alcohol and methyluvic acid.

Methyluvic acid is decomposed by prolonged boiling, yielding *dimethylketopentene*, $\mathrm{CO}<\begin{matrix}\mathrm{CH{=}CMe}\\ \mathrm{CHMe{\cdot}CH_2}\end{matrix}$ or  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH_2{\cdot}CHMe}\end{matrix}$, and on one occasion the author also observed the occurrence of a crystalline compound, which he regarded as an analogue of uvinone described by Paal and Dietrich (Abstr., 1887, 658). Dimethylketopentene boils at 118—119°; it is not miscible with water. W. C. W.

Succinic Acid and Ethyl Benzoylacetate. By A. SCHLOESSER (*Annalen*, **250**, 212—223).—Ethyl hydrogen phenythronate, $C_{13}H_9O_5Et$, is prepared by heating at 100° for 15 hours ethyl benzoylacetate (1 mol.), dry sodium succinate (1 mol.), and acetic anhydride (2 mols.). It crystallises in needles freely soluble in alcohol, ether, benzene, and chloroform, and melts when dry at 112·5°, but under water its melting point lies below 100°. The *calcium* salt, $(C_{15}H_{13}O_5)_2Ca + 3H_2O$, is deposited from alcohol in beautiful needles. It is less soluble in water than in alcohol. The *barium* salt, $(C_{15}H_{13}O_5)_2Ba + H_2O$, crystallises in rhombic plates, and is more soluble in water than the calcium salt.

The silver salt is amorphous. The salts of this acid are decomposed by boiling with baryta-water, yielding *barium phenythronate*, $C_{13}H_8O_5Ba + H_2O$. This salt is very soluble in water, but insoluble in alcohol. *Phenythronic acid*,  $\begin{matrix}\mathrm{CH(COOH)\cdot CH_2}\\ |\\ \mathrm{CPh : C(COOH)}\end{matrix}>\mathrm{CO}$, melts at 192—193°, and crystallises in silky needles. It is soluble in alcohol and in boiling water. The calcium salt contains 3 mols. H_2O. About 20 parts of water are required to dissolve one of the salt. The silver salt, $C_{13}H_8O_5Ag_2$, is an amorphous powder insoluble in water, but it becomes crystalline when rubbed with a glass rod. *Diethyl phenythronate*, $C_{13}H_8O_5Et_2$, melts at 44·5°, and forms rhombic crystals. When phenythronic acid is rapidly heated in a bent tube, a mixture of phenuvic acid and phenylketopentene distils over. *Phenuvic acid*,  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CPh}\\ |\\ \mathrm{CH_2\cdot CH\cdot COOH}\end{matrix}$, melts at 144—145°, and is freely soluble in alcohol, benzene, and light petroleum. The *calcium* salt, $(C_{12}H_9O_3)_2Ca + 2H_2O$, forms colourless needles. *Barium phenuvate*, $(C_{12}H_9O_3)_2Ba + H_2O$, dissolves more freely in water than the calcium salt. The silver salt is amorphous. *Phenylketopentene*,  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CPh}\\ |\\ \mathrm{CH_2\cdot CH_2}\end{matrix}$, crystallises in colourless prisms soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. It melts at 40°, and is identical with Paal's phenylmethylfurfuran (Abstr., 1885, 248).

W. C. W.

Effect of Thiophen and its Homologues on the Colour of the Derivatives of Benzene and its Homologues. By A. Bidet (*Compt. rend.*, **108**, 520—522).—The yellow tint of nitrobenzene and nitrotoluene, which becomes darker on exposure to light, is due to the presence of small quantities of nitrothiophen and its homologues, and if these are removed the nitrobenzene and nitrotoluene are practically colourless, and are not affected by light. They have, moreover, a much pleasanter odour than the ordinary preparations. Phenols free from thiophen-derivatives remain white. Pure aniline and its homologues are colourless when freshly distilled, and become yellow after some days, but never acquire the dark tint of ordinary aniline and toluidine. Pure aniline and toluidine mixed in the proportions necessary to give magenta, yield only a very small quantity of this dye when heated with arsenic acid. If, however, a small quantity of nitrothiophen is added, the ordinary yield is obtained.

The effect on the colour and other properties of the benzene compounds is a much more delicate test for thiophen than the ordinary isatin reaction.

Thiophen and its homologues may be removed by very careful fractionation, by repeated crystallisation, or by treatment with sulphuric acid. If nitrobenzene is dissolved in sulphuric acid, gently heated, and poured into water, and this process is repeated several times, the nitrothiophen remains in the aqueous acid. C. H. B.

Aromatic Nitriles. Benzyl Cyanide and Hydratroponitrile. By V. Meyer (*Annalen*, **250**, 118—125).—In benzyl cyanide, $CH_2Ph{\cdot}CN$, one hydrogen-atom can be displaced by benzyl, and in diphenylacetonitrile, $CH{\cdot}Ph_2CN$, the substitution can be even more easily accomplished, but in benzylphenylacetonitrile, $CHPhBz{\cdot}CN$, the hydrogen-atom cannot be displaced by benzyl. The hydrogen can also be displaced by benzyl in hydratroponitrile (methylbenzyl cyanide). Hydratroponitrile is most conveniently prepared by mixing benzyl cyanide with an equivalent quantity of freshly fused and powdered sodium hydroxide, methyl iodide is added, and the mixture gently warmed. The crude product of the reaction is distilled to separate benzyl cyanide and hydratroponitrile from the bye-products. When the nitriles are mixed with sodium ethoxide and benzaldehyde, the benzyl cyanide forms α-phenylcinnamonitrile which boils at 360°, and the benzylmethyl cyanide remains unaltered, and can easily be obtained in a pure state by fractional distillation.

Phenylcinnamonitrile is formed when a mixture of benzyl cyanide and benzyl chloride is boiled with solid sodium hydroxide.

W. C. W.

Replacement of the Methylene Hydrogen-atoms in Benzyl Cyanide. By H. Janssen (*Annalen*, **250**, 125—140).—By the action of benzyl cyanide (1 mol.) on solid sodium hydroxide (1 mol.) and benzyl chloride, a good yield of benzylbenzyl cyanide is obtained, but if the proportions of benzyl cyanide and sodium hydroxide are doubled, phenylcinnamonitrile, $CH{\cdot}Ph{:}C{\cdot}Ph{\cdot}CN$, is the chief product of the reaction. This nitrile is also formed when benzylbenzyl cyanide is treated with benzyl chloride and sodium hydroxide in molecular proportions. The conversion of benzylphenylacetonitrile into benzylphenylacetic acid by the action of strong hydrochloric acid at 130° is quantitative.

The cyanides obtained synthetically by the action of phosphorus pentachloride on benzylphenylacetamide from dibenzylcarboxylic acid and from α-phenylhydrocinnamic acid are identical with benzylbenzyl cyanide derived from benzyl cyanide.

Hydratropic acid can be prepared from acetophenone. For this purpose, strong hydrochloric acid (44 grams) is very slowly dropped on to pure potassium cyanide (30 grams) moistened with 30 drops of water, and covered with 50 grams of acetophenone. After an interval of 24 hours, the cyanhydrin, $OH{\cdot}CMePh{\cdot}CN$, is treated with hydriodic acid in sealed tubes at 150—160°. 30 grams of hydriodic acid and 1·7 grams of amorphous phosphorus are required for 10 grams of the cyanhydrin. The crude product is mixed with dilute sodium hydroxide solution, and on the addition of an acid to the alkaline solution, hydratropic acid is precipitated. The *amide* crystallises in plates, and melts at 91—92°. The nitrile boils at 230—232° without decomposition, and is soluble in alcohol and ether. The methine hydrogen-atom can be displaced by benzyl, yielding *benzylhydratroponitrile*, a yellow oil boiling at 335—337°. When heated with hydrochloric acid, it is converted into *benzylhydratropic acid*; this is freely soluble in alcohol and ether, crystallises in colourless needles, and melts at 126°. The *sodium* salt, $C_{16}H_{15}O_2Na + 7H_2O$, crystallises in needles, and melts in its water of crystallisation at 45°. It is soluble in alcohol. The silver and copper salts are insoluble in water, but the copper salt is soluble in alcohol and ether.

W. C. W.

Substituted Benzyl Cyanides. By K. NEURE (*Annalen*, **250**, 140—146).—Diphenylacetonitrile may be conveniently prepared from diphenylacetic acid obtained by the reduction of benzilic acid with hydriodic acid. The ammonium salt of diphenylacetic acid is prepared by passing dry ammonia gas into an ethereal solution of the acid. The ammonium salt is heated at 230° in sealed tubes to convert it into the amide, which is converted into the nitrile by the action of phosphorus pentachloride dissolved in phosphorus oxychloride. Benzyl chloride acts on an alcoholic solution of sodium and diphenylacetonitrile, yielding *benzyldiphenylacetonitrile*, $CPh_2Bz\cdot CN$. The new nitrile is freely soluble in chloroform, ether, benzene, and hot alcohol, and crystallises in plates or needles. It melts at 126°.

Methyldiphenylacetate is decomposed by sodium ethoxide with the formation of benzyl ethyl ether, methyl diphenylacetate, and diphenylacetic acid. Attempts to displace hydrogen by benzyl in benzophenone and triphenylacetonitrile led to negative results.

Benzyldiphenylacetonitrile is decomposed with difficulty, but by the action of a mixture of strong hydrochloric acid and acetic acids at 200—220°, it is partly converted into benzyldiphenylacetic acid. *Benzyldiphenylacetic acid* is soluble in ether, alkalis, and in hot alcohol, but it is very sparingly soluble in hot water, and is reprecipitated from alkaline solutions by the addition of an acid. It crystallises in needles, and melts at 162°. The author regards the compound which Meyer (Abstr., 1888, 702) obtained by the action of nitrous acid on diphenylacetonitrile as a polymeride of diphenylacetonitrile. This substance melts at 200—202°, and crystallises in needles.

Paratolylphenylacetonitrile, prepared by the action of phosphorus pentachloride on the amide of paratolylphenylacetic acid, crystallises in needles, melts at 59°, and is freely soluble in ether and in hot alcohol. It is converted into *benzyltolylphenylacetonitrile* by treatment with benzyl chloride and sodium ethoxide. The new nitrile melts at 121°, and is deposited from its alcoholic solution in white needles. The preparation of methylbenzyl cyanide has been described by V. Meyer (see preceding page). It is converted into methylphenylacetic acid, identical with hydratropic acid, by boiling with dilute sulphuric acid. *Ethylbenzyl cyanide* boils at 243—245°. On hydrolysis, it yields *ethylphenylacetic acid*, which melts at 42° and boils at 270—272°. The calcium salt crystallises in needles containing 2 mols. H_2O. The methyl salt boils at 228°.

Phenylcinnamonitrile is formed by the action of benzal chloride on benzyl cyanide in the presence of solid sodium hydroxide.

W. C. W.

Condensation of Benzyl Cyanide and its Substitution Products with Aldehyde and with Amyl Nitrite. By H. V. FROST (*Annalen*, **250**, 156—166).—*α-Phenylcinnamonitrile* is deposited as a crystalline mass when an alcoholic solution of sodium ethoxide is added to a mixture of benzyl cyanide (10 grams) and benzaldehyde (9·5 grams); it crystallises from boiling alcohol in white plates, melts at 86°, boils at 359—360° (corr.), and dissolves freely in ether, chloroform, benzene, carbon bisulphide, and in hot alcohol. It unites directly with two atoms of chlorine or bromine, forming compounds melting respectively at 129—130° and at 167—168°. *α-Phenylfurfuracrylonitrile*, $C_4H_3O{\cdot}CH{:}CPh{\cdot}CN$, prepared by the action of an alcoholic solution of sodium ethoxide on a mixture of benzyl cyanide and furfuraldehyde, melts at 42—43°; it unites with bromine to form a dibromide; this compound crystallises in six-sided plates of an orange colour, and melts at 113—114°. *α-Phenylanisacrylonitrile*, prepared from anisaldehyde and benzyl cyanide, forms white, needle-shaped crystals and melts at 93°.

The condensation product of benzyl cyanide with metanitrobenzaldehyde melts at 133—134°, and yields an unstable dibrom-additive product melting at 128°. The corresponding ortho-compound forms yellow needles and melts at 127—128°. The dibromide is unstable and melts at about 129° with decomposition. α-Phenylparanitrocinnamonitrile melts at 117—118°. It does not form additive compounds with chlorine and bromine. Parabromobenzyl cyanide forms crystalline condensation products with benzaldehyde, furfuraldehyde and anisaldehyde. These compounds melt at 111—112°, 65°, and 135° respectively. Substitution takes place when bromine is added to a solution of α-parabromophenylanisacrylonitrile, and a compound is formed of the composition $C_{16}H_{11}NOBr_2$. It is probably either $OMe{\cdot}C_6H_3Br{\cdot}CH{:}C(C_6H_4Br){\cdot}CN$ or $OMe{\cdot}C_6H_4{\cdot}CH{:}C(C_6H_3Br_2){\cdot}CN$.

The sodium salt of isonitrosobenzylcyanide is deposited as a crystalline mass, on mixing together equivalent quantities of benzyl cyanide, amyl nitrite, and an alcoholic solution of sodium ethoxide. Isonitrosobenzyl cyanide has been recently described by A. Meyer (Abstr., 1888, 693). Parabromisonitrosobenzyl cyanide crystallises in plates and melts at 131—132°. It forms amorphous sodium, silver, and copper salts. W. C. W.

Action of Chlorine and Bromine on Benzyl Acetate and similar Substances. By E. Seelig (*J. pr. Chem.* [2], **39**, 157—187).—78 per cent. of the theoretical yield of benzyl acetate is obtained by heating benzyl chloride (150 grams) with fused sodium acetate (97·6 grams) and glacial acetic acid (200 grams) for 25 hours. With ammonia, benzyl acetate forms benzyl alcohol and acetamide; chlorine acts on it between 130° and 170°, forming acetic and benzoic chlorides; in the presence of powdered ferric chloride, parachlorobenzyl chloride is obtained in the cold. Bromine decomposes benzyl acetate in the cold, forming para- and ortho-bromobenzyl bromide, and the substance $C_2H_4O_2Br_2$, described by Mühlhäuser and Hell (Abstr., 1879, 705); near the boiling point, acetic and benzoic bromides are formed.

Parabromobenzyl acetate melts at 32° and boils at 260—263°; bromine acts on it near the boiling point, forming bromobenzyl bromide.

Neither chlorine nor bromine act on ethyl benzoate or ethyl acetate below 100°; at higher temperatures the latter yields, with chlorine, benzoic and acetic chlorides respectively, together with aldehyde.

With chlorine, in the cold, phenyl acetate yields acetic chloride, chlorophenol, and chlorophenyl acetate; when heated, dichlorophenyl acetate is the chief product; in the presence of ferric chloride, trichlorophenyl acetate is also formed in the cold. The action of bromine is analogous.

Benzyl acetate is converted into acetic acid and benzyl chloride by hydrogen chloride at 180°, and ethyl benzoate into benzoic acid and ethyl chloride.

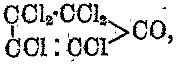
The author has already discussed the action of chlorine on toluene (Abstr., 1887, 362); he concludes with some general deductions as to the position in organic compounds of the hydrogen which is most easily attacked by the halogens. A. G. B.

Action of Chlorine on Catechol and Orthamidophenol. By T. Zincke and F. Küster (*Ber.*, 22, 486—497). The hexachlorodiketohexene obtained from catechol or orthamidophenol (compare Abstr., 1888, 1277) is identical with the compound formed when tetrachlororthoquinone is treated with chlorine. The difference in the melting points which was previously observed is due to the presence of varying quantities of water; the compound $C_6Cl_6O_2,2H_2O$ readily loses water when recrystallised from a mixture of ether and benzene, its melting point being thereby raised and only becoming constant when the compound $C_6Cl_6O_2,H_2O$, which does not lose water when recrystallised from hot benzene, is formed.

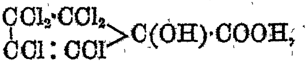
Propylideneacetic acid is obtained when pentachlorobutenecarboxylic acid is dissolved in dilute alkali and treated with 40 to 50 times its weight of 4 per cent. sodium amalgam, the whole being warmed for a long time to complete the reaction; the alkaline solution is first shaken with ether, then acidified and the acid extracted with ether and purified by fractional distillation. The yield is about 50 per cent. of the calculated quantity. It combines with bromine, yielding an oily bromide, and is identical with the propylideneacetic acid prepared by Komnenos (Abstr., 1884, 422). The *barium* salt, $(C_4H_7\cdot COO)_2Ba$, melting at 265—270°, and the *calcium* salt, with $1H_2O$, are readily soluble in water, alcohol, and ether. The *copper* salt is a greenish, crystalline compound, melting at 91°. The *silver* salt separates from hot water in moss-like crystals. The *mercuric* salt crystallises in needles.

The reduction of pentachlorobutenecarboxylic acid to propylideneacetic acid shows that the constitution of the former is

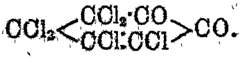
$$CCl_2{:}CCl\cdot CCl{:}CCl\cdot COOH,$$

the constitution of hexachloroketopentene is therefore  $\begin{matrix}CCl_2\cdot CCl_2\\ |\\ CCl:CCl\end{matrix}\!>\!CO$,

that of hexachlorohydroxypentenecarboxylic acid,



$$\begin{matrix}CCl_2\cdot CCl_2\\ |\\ CCl:CCl\end{matrix}\!>\!C(OH)\cdot COOH,$$

and that of hexachlorodiketohexene,  $CCl_2\!<\!\begin{matrix}CCl_2\cdot CO\\ CCl{:}CCl\end{matrix}\!>\!CO.$

The conversion of catechol and orthamidophenol first into tetrachlororthoquinone and then into propylideneacetic acid proves that orthoquinone has the diketone constitution, and is also evidence in support of Kekulé's benzene formula. F. S. K.

Orthonitroethylaniline and its Derivatives. By A. HEMPEL (*J. pr. Chem.* [2], **39**, 199—200).—*Orthonitroethylaniline*,

$$NO_2 \cdot C_6H_4 \cdot NHEt,$$

is obtained by heating orthonitrophenyl ethylene ether with alcoholic ethylamine at 140°; it is an orange-red oil, distilling with decomposition and is precipitated unchanged on adding water to its solution in acids. *Dinitroethylaniline*, $C_6H_3(NO_2)_2 \cdot NHEt$, is obtained by the action of nitrous acid on an ethereal solution of orthonitroethylaniline; it forms lemon-yellow needles melting at 113—114°. *Orthonitronitrosoethylaniline* is formed when sodium nitrite is added to a hydrochloric acid solution of orthonitroethylaniline; it crystallises in long, yellow needles melting at 32°. *Orthamidoethylaniline*, $NH_2 \cdot C_6H_4 \cdot NHEt$, is a colourless oil boiling at 249° and becoming dark-red in air. *Orthamidoethylacetanilide*, $C_6H_4 \cdot N_2H_2EtAc$, obtained when acetic anhydride acts on an ethereal solution of orthamidoethylaniline, forms white crystals melting at 104°. *Ethenylorthoethylphenylenediamine*,

$$C_2H_3 < \begin{matrix} N— \\ NEt \end{matrix} > C_6H_4,$$

crystallises from alcohol in slender, colourless, rhombic tables or prisms, melting at 178°. A. G. B.

Last Runnings obtained in the Purification of Aniline and Toluidine. By C. HELL and T. ROCKENBACH (*Ber.*, **22**, 505—514). —The dark oil which is obtained when the last runnings in the purification of aniline are acidified with hydrochloric acid and distilled with steam, consists of a variety of compounds which cannot be separated by fractional distillation. When boiled with a 5 per cent. solution of potassium permanganate, it yields various organic acids which remain in solution, and an oily product insoluble in water. After removing the supernatant oil and adding excess of sulphuric acid, a mixture of acids is precipitated from which by repeated fractional crystallisation of the lead and silver salts, terephthalic acid and a small quantity of an acid melting at 228—232° were isolated. The latter crystallises in shining needles, and probably has the composition $C_{10}H_{10}O_4$. The mother-liquors from these acids contain small quantities of acetic acid and its next higher homologues, which can be separated by distilling with steam; in one experiment, paratoluic acid was isolated from the non-volatile residue. The oily oxidation product yielded, on keeping, a crystalline substance, from which, by recrystallising from ether and absolute alcohol, two compounds, one melting at 122·5°, probably a sulphone or sulphone-derivative, the other melting at 66°, were isolated. The mother-liquors from the crystalline products can be separated by fractional distillation into a large portion boiling at 255—259°, and a somewhat smaller fraction boiling at 259—264°, The fraction 255—259° consists of a *hydrocarbon*, $C_{14}H_{22}$, in an almost pure condition. This hydrocarbon becomes gelatinous when cooled with a mixture of ether and solid carbonic anhydride, and when heated at 220° with concentrated nitric acid, it yields terephthalic acid. When boiled with a mixture of nitric acid and sulphuric acid, it yields a brown, oily nitro-compound, together with small quantities of a colourless, crystalline substance melting at 228°. The oily nitro-compound, when reduced with tin and hydrochloric acid, is converted into a white, amorphous *base*, which rapidly darkens in colour and is soluble in ether. The *hydrochloride* of this base is a semi-crystalline compound, which quickly turns dark violet; the *platinochloride*, $(C_{14}H_{21}NH_2)_2,H_2PtCl_6$, is a brown powder.

The *barium* salt, $(C_{14}H_{21}SO_3)_2Ba + H_2O$, is obtained in an impure condition when the hydrocarbon is treated with a mixture of ordinary and fuming sulphuric acid, and the acid isolated by neutralising with barium carbonate, filtering, and evaporating. The free *acid*, $C_{14}H_{21}SO_3H$, is an olive-green liquid, which dissolves in water with a greenish colour. The *lead* salt crystallises with 1 mol. H_2O. When the hydrocarbon is heated with bromine, it yields a syrupy mixture of various substances, from which a colourless, crystalline, *bromo-derivative*, $C_{14}H_{20}Br_2$, separates after a long time; with excess of bromine, a syrupy compound, $C_{14}H_{19}Br_3$, is formed.

The oil, obtained in like manner from the last runnings in the purification of toluidine, was investigated in the same way. The products obtained were the same as those described above, except that no neutral, crystalline substance was isolated, and the crystalline nitro-compound (m. p. 228°) was not formed on nitrating the hydrocarbon.

These results show that the neutral compounds which form the subject of this investigation contain small quantities of sulphur compounds, but consist principally of aromatic hydrocarbons containing two side chains in the para-position, one of which, as shown by the production of paratoluic acid, contains only one carbon-atom.

Pure terephthalic acid is best isolated from the mixture of acids which is so often obtained on oxidising aromatic compounds, by the following method:—The crude acid mixture is neutralised with ammonia, the solution precipitated with lead or silver nitrate, the precipitate boiled several times with water, decomposed with ammonium or sodium carbonate, and the acid precipitated from the filtered, alkaline solution by adding nitric acid; this process is repeated several times. The acid is then boiled for a long time with water and lead carbonate, the whole filtered, the residue washed with hot water, treated with ammonium carbonate, the acid precipitated from the filtered, alkaline solution, washed, and converted into the strontium salt. The filtrate from the latter contains the more readily soluble salts of the other acids and small quantities of strontium terephthalate, which can be separated by concentrating the solution. *Strontium terephthalate*, prepared by boiling the acid with strontium carbonate and a large quantity of water, crystallises in plates, and is very sparingly (1 : 524·4 at 17°) soluble in water. The *zinc* salt is a white, granular compound; the *cadmium* salt is crystalline. F. S. K.

Action of Sulphur on Toluidine. By L. GATTERMANN (*Ber.*, 22, 422—426).—Duisberg and Pfitzinger (communication to the author) investigated the yellow dye known as primuline, and found that it differed in all respects from the thioparatoluidine described by Dahl and Co. (D. R.-P., No. 35,790) (compare Jacobson, this vol., p. 498). They found that the latter is moderately easily soluble in alcohol, from which it crystallises in colourless needles melting at 191°, whereas the mother-substance of primuline is an intensely yellow, amorphous powder, very sparingly soluble in alcohol, and yields solutions showing a greenish-yellow fluorescence. The sulphonic acids, alkaline sulphonates, and the diazo-compounds of these two thio-bases also differ both in their chemical and physical properties.

The author heated paratoluidine (100 grams) with sulphur (60 grams) at 185° for about 24 hours, and, after distilling the unchanged toluidine with steam, extracted the residue with dilute alcohol, thereby obtaining a compound, $C_{14}H_{12}N_2S$, identical with that prepared in like manner by Jacobson (*loc. cit.*). Its molecular weight, determined by Raoult's method, was found to be 232·3 as a mean of two experiments. When treated with nitrous acid in boiling alcoholic solution, it yields a compound, $C_{14}H_{11}NS$, which crystallises from alcohol in colourless needles, melts at 118—119°, and is not acted on by acetic chloride or methyl iodide. When distilled with zinc-dust, it yields paratoluidine, and it forms an additive compound with bromine in glacial acetic acid solution.

The base, insoluble in alcohol, which is the real mother-substance of primuline, is best purified by crystallisation from naphthalene. It is thus obtained in the form of a yellow, crystalline powder, and seems to have the composition $C_{14}H_{10}N_2S_2$.

Orthotoluidine also yields a thio-base when heated with sulphur. This substance crystallises from alcohol in yellow plates, melts at 120°, and has the same composition as that obtained from paratoluidine. With bromine it forms an additive compound, $C_{14}H_{12}SBr_2$, which crystallises from glacial acetic acid in yellow needles, melts at 190°, and is not decomposed when boiled with potash. When treated with nitrous acid in alcoholic solution, it yields a basic substance which crystallises from alcohol in long needles melting at 48° (compare Green, Trans., 1889, 227). F. S. K.

Behaviour of some Primary Aromatic Amines towards Sulphur. By R. ANSCHÜTZ and G. SCHULTZ (*Ber.*, 22, 580—586).—The base, $C_{14}H_{12}N_2S$ (diamidostilbene sulphide), is obtained when paratoluidine (2 mols.) is heated with sulphur (4 atoms) (compare Jacobson, this vol., p. 498, and Gattermann, preceding Abstract). It yields an *acetyl*-derivative, $C_{14}H_{11}N_2SAc$, which crystallises from alcohol in small, yellowish prisms melting at 225°.

Diamidodimethylstilbene sulphide, $C_{16}H_{16}N_2S$, is best prepared by heating a mixture of amidometaxylene (400 grams) and sulphur (100 grams) at 185—195° until the evolution of hydrogen sulphide ceases. The product is dissolved in moderately concentrated sulphuric acid, the solution gradually diluted, and the precipitate separated, washed, and decomposed with soda. The base is then distilled, the distillate dissolved in moderately strong sulphuric acid, the solution diluted, and the sulphate recrystallised from dilute alcohol. The free base crystallises from alcohol in yellowish-white prisms, melts at 107°, boils at 282—284° (13—14 mm.). and is readily soluble in hot alcohol, but only sparingly in cold alcohol, and insoluble in water. It yields azo-compounds, amongst others "Erika," which dye cotton-wool directly in a sodium sulphate bath.

The *acetyl*-derivative, $C_{16}H_{15}N_2SAc$, crystallises from alcohol in small, colourless needles, melts at 227°, and is insoluble in water, but readily soluble in glacial acetic acid and boiling benzene. The *bromo*-derivative, $C_{16}H_{16}N_2SBr_2 + CHCl_3$, separates in crystals when the thio-base is treated with bromine in chloroform solution; it loses its chloroform at 100°, and decomposes without melting when heated at a higher temperature. The thio-base yields a sulphonic acid, the sodium salt of which is colourless; the latter combines with vegetable fibres, to which it imparts a blue fluorescence. The sulphonic acid can be diazotised in the vegetable fibres, and combined with naphthol or naphtholsulphonic acids.

The *base*, $C_{16}H_{16}N_2S$, obtained in like manner from amidoparaxylene, crystallises from alcohol in long, yellowish needles melting at 144°. It yields an *additive* compound with bromine, and the *acetyl*-derivative, $C_{16}H_{15}N_2SAc$, melts at 212°. The azo-compounds derived from this base do not dye cotton-wool.

Two thio-bases, having the composition $C_{18}H_{20}N_2S$, are formed when ψ-cumidine (3 to 4 parts) is heated with sulphur at 185—195° until evolution of gas ceases. If the product is treated with alcohol, the larger part dissolves, and there remains a lemon-yellow powder which separates from hot alcohol or hot benzene in small, yellow, nodular crystals, melting at 183°. The mixture of bases obtained on evaporating the alcoholic solution is treated with sulphuric acid, the salts extracted with boiling water, recrystallised from alcohol, and decomposed with alkali. When the free bases are recrystallised from alcohol, the compound melting at 183° separates first, and then a readily soluble base, which crystallises in yellowish needles melting at 125°.

F. S. K.

Preparation and Properties of Paraxylidine. By O. N. Witt, E. Nölting, and S. Forel (*Chem. Centr.*, 1889, 253—254, from *Bull. Soc. indust. Mulhouse*, **58**, 630—635).—Paraxylidine is best obtained from commercial xylidine as follows: The xylidine is added gradually to fuming sulphuric acid, containing 15—20 per cent. of sulphuric anhydride, in such proportion that exactly 1 mol. of xylidine is used with each mol. of sulphuric anhydride. The mixture is heated for some time on the water-bath, allowed to cool, and then treated with water. The sparingly soluble metaxylidinesulphonic acid is precipitated, the mother-liquor is neutralised with lime, and from the calcium salt thus obtained the sodium salt is prepared, which separates from the solution on concentration.

In order to prove that a true para-derivative had been prepared, the authors prepared the diazo-sulphate and from it the iodo-xylene, and from this, by reduction with sodium amalgam, the corresponding xylene. The latter proved to be paraxylene.

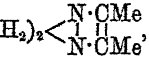
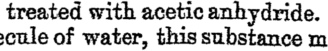
Other derivatives obtained were:—*Nitroacetylparaxylidine*, melting at 166°; *nitroxylidine* melting at 142°, obtained from the last-named compound; and *diamidoxylidine* melting at 146·5—147°.

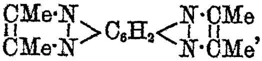
J. W. L.

Symmetrical Tetramidobenzene. By R. NIETZKI and E. MÜLLER (*Ber.*, **22**, 440—450).—*Tetracetyltetramidobenzene*, [$(NHAc)_4$ = 2 : 3 : 5 : 6], is obtained when tetramidobenzene hydrochloride is warmed with sodium acetate and acetic anhydride. It crystallises in long, colourless needles, melts at 285°, and is reconverted into tetramidobenzene when hydrolysed with concentrated hydrochloric acid. When hydrolysed with potash, it loses 1 mol. H_2O, and is converted into triacetylethenyltetramidobenzene.

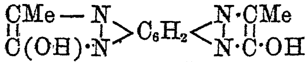
The compound $C_8H_6N_4O_2$ separates in the form of a greenish, amorphous precipitate when carbonyl chloride is passed into a concentrated aqueous solution of tetramidobenzene hydrochloride. It is almost insoluble in all neutral solvents, but has distinct acid properties, dissolving in dilute potash, forming a yellowish-green solution, from which it is precipitated on adding acids.

The corresponding thio-compound, $C_8H_6N_4S_2$, prepared by heating tetramidobenzene hydrochloride with sodium acetate and carbon bisulphide in alcoholic solution, is a dirty white powder, which is only soluble in alkalis.

Dimethyldiamidoquinoxaline,  $C_6H_2(NH_2)_2<\begin{matrix}N\cdot CMe\\ | \quad \| \\ N\cdot CMe\end{matrix}$, separates immediately when an aqueous solution of diacetyl is added to a solution of tetramidobenzene hydrochloride in presence of sodium acetate. It crystallises from hot water in long, orange-yellow needles, sublimes at 130° with partial decomposition, but without melting, and has only feeble basic properties. It crystallises from alcohol with 1 mol. of alcohol, which is not driven off at 100°, and the crystals from water, when dried at 100°, retain 1 mol. H_2O, which cannot be expelled without decomposing the substance. It dissolves in hydrochloric acid with a red coloration, and in concentrated sulphuric acid, forming a violet solution, which on diluting first turns red and then orange. A compound, $C_{14}H_{16}N_4O_2$, is formed when dimethyldiamidoquinoxaline is treated with acetic anhydride. As the quinoxaline contains one molecule of water, this substance may possibly be the acetyl-anhydro-base,  $\begin{matrix}CMe\cdot N\\ \| \qquad | \\ CMe\cdot N\end{matrix}>C_6H_2<\begin{matrix}NAc\\ \\ —N\end{matrix}\geqslant CMe$; this view is rendered more probable by the fact that when hydrolysed with alkalis it yields a new, moderately strong base, which dissolves in acids with a deep-red coloration.

Tetramethyldiquinoxaline,  $\begin{matrix}CMe\cdot N\\ \| \qquad | \\ CMe\cdot N\end{matrix}>C_6H_2<\begin{matrix}N\cdot CMe\\ | \quad \| \\ N\cdot CMe\end{matrix}$, obtained by warming tetramidobenzene with excess of diacetyl, crystallises from hot aniline in reddish plates, melts above 300°, and sublimes in small, glittering plates. It is only very sparingly soluble in water, alcohol, and ether, but moderately easily in glacial acetic acid, yielding a solution which turns blue on adding mineral acids, very small quantities of a highly unstable salt separating after a long time. It dissolves in concentrated sulphuric acid with a bluish-green coloration, which becomes blue on adding water.

Dimethyldihydroxydiquinoxaline,



$$\begin{array}{l}\mathrm{CMe - N}\\ \mathrm{C(OH)\cdot N}\end{array}\!\!>\mathrm{C_6H_2}<\!\!\begin{array}{l}\mathrm{N\cdot CMe}\\ \mathrm{N\cdot C\cdot OH}\end{array}$$

prepared by heating a solution of tetramidobenzene hydrochloride with sodium acetate and excess of pyruvic acid, is sparingly soluble in neutral solvents, but dissolves freely in dilute alkalis, forming yellowish-green, fluorescent solutions. A yellow, crystalline *potassium* salt separates when the solution in potash is kept for a long time.

Diamidodiphenylquinoxaline, $C_{20}H_{16}N_4$, is precipitated together with tetraphenyldiquinoxaline when tetramidobenzene hydrochloride is warmed with benzile and sodium acetate in alcoholic solution. It is isolated and purified by extracting the precipitate with 50 per cent. alcohol, mixing the alcoholic solution with very dilute nitric acid, and decomposing the reddish-brown, crystalline nitrate which is precipitated on standing. It crystallises from dilute alcohol in yellow plates, melts at 245°, and yields a yellow, crystalline *diacetyl-*derivative.

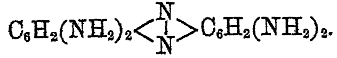
Tetraphenyldiquinoxaline, $C_6H_2(N_2C_2Ph_2)_2$, remains after extracting the diphenylquinoxaline with dilute alcohol. It melts at 289°, and dissolves in concentrated sulphuric acid, yielding a blue solution which turns first red and then orange on adding water. It is readily soluble in hot glacial acetic acid, but frequently separates from the boiling solution in needles, and is then very sparingly soluble in this solvent; if, however, a few drops of hydrochloric acid are added, it dissolves freely, forming a dark-green solution.

The *acetate* of a base, $C_{12}H_{12}N_6$, separates in green needles when air is passed for two to three hours through an aqueous (200 c.c.) solution of tetramidobenzene hydrochloride (10 grams) and sodium acetate (20 grams) (compare Nietzki and Hagenbach, Abstr., 1887, 476). The free *base,* prepared by decomposing the red, aqueous solution of the salt with alkali, crystallises from alcohol in long, brown needles, and from boiling aniline in yellow needles containing aniline. It is only moderately soluble in hot water, alcohol or aniline, the solutions showing a yellowish-green fluorescence. It dissolves in acetic acid with a bluish-violet colour, which changes to red on boiling, but again turns bluish-violet when the solution is cooled; a similar change in colour takes place on diluting with water. The solution in concentrated sulphuric acid is yellow, but, on diluting, it passes through blue and violet, becoming first red and finally yellow. This compound has only feeble basic properties, and, when heated above 130°, it loses (approximately) one molecule of ammonia. The *nitrate,* $C_{12}H_{12}N_6,2HNO_3 + 2H_2O$, separates in slender, green needles when nitric acid is added to a solution of the acetate; it loses nitric acid when heated at 50°, but does not lose its water over sulphuric acid. The *sulphate* crystallises in green needles, the *hydrochloride* in copper-red plates. The salts all dissolve in a small quantity of water with a magenta coloration, the solutions showing a yellow fluorescence, but on diluting strongly the colour suddenly changes to yellow. Dilute solutions colour silk or wool a red shade, which is turned violet by acids and yellow by alkalis. The *tetracetyl*-derivative, $C_{12}H_8N_6Ac_4$, is an orange-yellow powder, insoluble in all neutral solvents.

Phenanthraquinone when added to a glacial acetic acid solution of the base, produces a green, crystalline precipitate, which is insoluble in all neutral solvents, but dissolves in concentrated sulphuric acid with a deep bluish-green colour, which changes to violet-red and orange on adding water.

Benzile also gives a green precipitate, insoluble in neutral solvents, but soluble in sulphuric acid, yielding a blue solution which turns green, red, and finally orange on diluting; this compound is formed by the combination of one molecule of the base with two molecules of benzile.

The constitution of this base, which from its behaviour is clearly a eurhodine-derivative, is most probably



$$C_6H_2(NH_2)_2<\overset{N}{\underset{N}{|}}>C_6H_2(NH_2)_2.$$

F. S. K.

Short Communications. By P. Friedländer (*Ber.*, **22**, 587—591).—An amido-group is best eliminated by treating an alkaline solution of the corresponding diazo-compound with a solution of stannous chloride in aqueous soda. In the case of aniline, for example, the process is best carried out as follows:—The aniline is converted into diazobenzene chloride, and the dilute (1 : 10 to 1 : 20) slightly acid solution of the latter poured into well-cooled soda and mixed with a solution of stannous chloride in aqueous soda. Nitrogen is rapidly evolved, and the benzene which is formed collects on the surface of the liquid.

α-Naphthylamine and sulphanilic acid can be readily converted into naphthalene and benzenesulphonic acid respectively by the same method, but this reaction should be more especially employed in the case of compounds which yield products insoluble in soda.

Ethylbenzylaniline is prepared on the large scale by heating ethylaniline with benzyl chloride. It is, when pure, a colourless oil, boiling at 285—286° (uncorr.; 710 mm.) with slight decomposition, and is readily soluble in most ordinary solvents but insoluble in water. It behaves towards benzaldehyde in the same way as dimethylaniline. The *hydrochloride* and the *sulphate* are oily compounds. The *platinochloride*, $(PhNEt{\cdot}CH_2Ph)_2,H_2PtCl_6$, crystallises from dilute hydrochloric acid in small, light-yellow needles.

Diethyldibenzyldiamidotriphenylmethane, $CHPh(C_6H_4{\cdot}NEt{\cdot}CH_2Ph)_2$, is obtained when ethylbenzylaniline is heated at 100—110° for several hours with dehydrating agents, such as zinc chloride, sulphuric acid, or anhydrous oxalic acid. It crystallises from acetone in colourless needles, melts at 115—116°, and is readily soluble in benzene, acetone, and glacial acetic acid, but only sparingly in alcohol and light petroleum, and insoluble in water. When warmed with chloranil in alcoholic acetic acid solution, it yields a dye, insoluble in water, which in properties resembles malachite-green, but has a much more distinct yellowish shade. When warmed with fuming sulphuric acid, it yields a mixture of readily soluble di- and tri-sulphonic acids, which are precipitated almost entirely as a resinous mass on adding sodium sulphate to the aqueous solution. If this product is treated with the calculated quantity of lead peroxide, readily soluble, intensely green sulphonic acids are obtained, the sodium salts of which, in the dry state, are commercially known as "acid-green" (compare Mühlhäuser, Abstr., 1887, 579).

Ethylbenzylaniline and paranitrobenzaldehyde yield a yellow, crystalline nitroleuco-base, from which by reducing, sulphonating, and oxidising "acid-violet" (sulphonic acids of paramidodiethyldibenzyldiamidotriphenylcarbinol) is obtained.

When pure amidoazonaphthalene is reduced with stannous chloride in acid solution, naphthylenediamine and naphthylamine are obtained, but no pyridine is formed, as stated by Perkin and Church (this Journal, 1863, 207).

Amidoazonaphthalene (compare Lecco, this Journal, 1875, 169) is best prepared by mixing α-diazonaphthalene chloride (1 mol.) with naphthalene hydrochloride (1 mol.) in cold, aqueous solution, and then neutralising with sodium carbonate. The product separates in yellowish-brown flocks, and can be obtained in brownish-red needles, with a green reflex, by recrystallisation from xylene. The yield is theoretical. F. S. K.

Isomerism of Oximido-compounds. Isomeric Mono-substituted Hydroxylamines. By E. Beckmann (*Ber.*, 22, 429—440 compare Abstr., 1888, 55, and also *Ber.*, 21, 1163).—β-Benzaldoxime crystallises from glacial acetic acid unchanged, and its molecular weight determined by Raoult's method with this solvent is 123 as the average of four experiments; it is therefore isomeric with α-benzaldoxime. The β-oxime is most readily obtained from the α-compound by passing hydrogen chloride into an ethereal solution of the latter, and decomposing the precipitated hydrochloride with sodium carbonate solution.

When α-benzaldoxime (6 grams) is heated with a mixture of glacial acetic acid (24 grams) and acetic anhydride (6 grams), saturated with hydrogen chloride, it is first converted into the β-oxime, the latter is then decomposed, yielding considerable quantities of benzamide and benzonitrile, together with small quantities of benzaldehyde.

α-Benzaldoxime forms a sodium-derivative (compare Petraczek, Abstr., 1883, 569). The β-oxime dissolves in a saturated alcoholic solution of sodium ethoxide, and on adding ether, a crystalline precipitate of the sodium-derivative, $CHPh\colon NONa$ is produced.

The α- and the β-oxime both form oily *ethyl*-derivatives when treated with sodium ethoxide and ethyl iodide. These compounds are decomposed when heated with concentrated hydrochloric acid at 100°, being in both cases almost entirely converted into benzoic acid, ammonium chloride, and ethyl chloride.

The α-oxime yields an oily *benzyl*-derivative, $CHPh\colon NO\cdot C_7H_7$, which is insoluble in concentrated hydrochloric acid, but when heated with this acid at 140°, it yields benzyl chloride, benzoic acid, and ammonium chloride. Under certain conditions, however, for instance when warmed for a short time with a dilute alcoholic solution of hydrogen chloride, it is partially converted into benzaldehyde and benzylhydroxylamine hydrochloride, identical with the compound obtained by Janny (Abstr., 1883, 581).

β-Benzylbenzaldoxime crystallises from ether, in which it is moderately soluble, in small needles, melts at 81—82°, and is not acted on when treated with benzyl chloride and sodium ethoxide. It forms a *hydrochloride*, $C_{14}H_{13}NO,HCl$, melting at 146—148°, which dissolves freely and without decomposition in warm, concentrated hydrochloric acid. When heated with a large quantity of concentrated hydrochloric acid, this salt is readily decomposed into benzaldehyde and β-benzylhydroxylamine hydrochloride.

β-Benzylhydroxylamine hydrochloride, $C_7H_7O{\cdot}NH_2,HCl$, is totally different from the corresponding salt obtained by decomposing the α-compound. It crystallises in needles, is readily soluble in cold alcohol, and melts at 109—111°. It reduces Fehling's solution in the cold, and when digested with benzaldehyde and sodium hydrogen carbonate in alcoholic solution, is converted into β-benzylbenzaldoxime.

These results show that the isomerism of oximido-compounds may be due to a different arrangement in space of the atoms constituting the oximido-group. F. S. K.

Isomerism of Oximido-compounds. By E. Beckmann (*Ber.*, **22**, 514—517).—α-Benzylbenzaldoxime yields but little benzylhydroxylamine hydrochloride when warmed with dilute alcoholic hydrochloric acid, but when α-benzylbenzaldoxime (1 part) in small quantities (5 to 15 grams) is treated in the cold with concentrated aqueous hydrochloric acid (5 parts), and a saturated absolute alcoholic solution of hydrogen chloride (5 parts), benzylhydroxylamine hydrochloride separates in a few hours (compare preceding Abstract); 10 grams of the oxime yield about 1·5 grams of the pure salt. This salt is identical with that obtained from benzylacetoxime, and when treated with benzaldehyde, it yields a benzylbenzaldoxime identical with the compound obtained by the action of benzyl chloride on sodobenzaldoxime.

The isomerism of α- and β-benzaldoxime is, therefore, due to a difference in the constitution of the oximido-groups.

α-Benzylhydroxylamine is an oil; the β-compound crystallises from light petroleum in needles melting at 56—58°.

When benzile is warmed with hydroxylamine hydrochloride and sodium hydrogen carbonate, in alcoholic solution, a monoxime is obtained totally different from the compound (m. p. 134—135°) previously described by Wittenberg and Meyer (Abstr., 1883, 803) and Meyer and Oelkers (Abstr., 1888, 703). This oxime separates from alcohol, ether, and light petroleum in an oily condition, but gradually solidifies to colourless needles. It crystallises from benzene, melts at about 88°, and when treated with hydrogen chloride in ethereal solution, yields a colourless, crystalline salt from which, on decomposing with sodium carbonate, what seems to be the original oxime (m. p. about 88°) is obtained. F. S. K.

Isomerism of Oximido-compounds. Isomeric Monosubstituted Hydroxylamines. By K. AUWERS and V. MEYER (*Ber.*, **22**, 564—567).—The authors are of the opinion that although Beckmann's view of the isomerism of the two benzaldoximes (compare this vol., p. 607) may very probably be correct, even if proved to be so, it would not invalidate their conclusions regarding the isomerism of the benziloximes (compare Auwers and Meyer, this vol., p. 611).

α-Benziledioxime yields two benzyl-derivatives which, in their properties, show complete analogy to the two dimethyl-derivatives of the α-dioxime. The one melts at 104—105°, combines with concentrated hydrochloric acid, and yields benzile when heated at 100° with concentrated hydrochloric acid. The other melts at 153—154°, does not combine with hydrochloric acid, and is converted into the corresponding dibenzyl-derivative of β-benziledioxime when treated with hydrochloric acid at 100°. The last-named compound melts at 59—60°, and is formed in considerable quantities when β-benziledioxime is treated with soda and benzyl chloride.

When benzile in alcoholic solution is digested with benzylhydroxylamine hydrochloride a benzylbenzilemonoxime is obtained; this compound melts at 114—115°, and differs from the benzyl-derivative (m. p. 94°) prepared from α-benzilemonoxime.

Phenanthraquinonedioxime crystallises in yellowish, microscopic prisms melting at 194°. F. S. K.

Manufacture of Benzyl-violet. By O. MÜHLHÄUSER (*Dingl. polyt. J.*, **270**, 179—181).—Commercial benzyl-violet is mainly composed of pentamethylbenzylpararosaniline hydrochloride. It contains also the hydrochloride of hexamethyl-, and at times of tetramethyl-dibenzyl pararosaniline. It is formed by the action of benzyl chloride (1 mol.), on pentamethylpararosaniline (1 mol.). The preparation involves the benzylation of methyl-violet, separation of the crude violet and its purification. The first operation is effected in cast-iron enamelled pots fitted with upright condensers and stirrers, and surrounded by a steam and cold water jacket. The pots are charged with 25 kilos. of alcohol (90 per cent.), and 30 kilos. of powdered methyl-violet. The mixture is then heated to boiling, in order to dissolve the violet, after which it is cooled to 60°, treated with 18 kilos. of benzyl chloride, and agitated for half an hour. 24 kilos. of soda ley of 30° B. is then added, and the mass heated for four hours at 80° in a reflux apparatus. The contents are diluted with 50 litres of water, heated to expel the alcohol and other volatile products, and neutralised with hydrochloric acid in a suitable vessel. The solution is passed through a woollen filter, and the colouring matter precipitated by the addition of salt solution. The product is purified by solution in water, filtration, and reprecipitation with salt. The violet is then collected, dehydrated at 55° in copper pans, and ground up in a mill. It forms a pale-green powder. D. B.

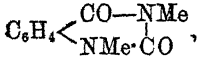
Benzoylenecarbamide (Uramidobenzoyl). By W. ABT (*J. pr. Chem.* [2], **39**, 140—155).—Benzoylenecarbamide may be prepared by heating orthamidobenzamide with carbamide (equal mols.) at 200°.

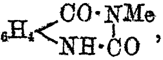
When orthamidobenzamide (2 mols.) is digested with ethyl chlorocarbonate in ether, *carboxyethylorthamidobenzamide*,

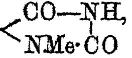
$$NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}COOEt,$$

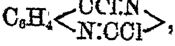
is obtained; it crystallises in long, white needles, little soluble in water, but soluble in other solvents, and melts at 152—153°, above which temperature it is converted into benzoylenecarbamide.

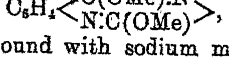
An *α-sodium*-derivative of benzoylenecarbamide has been obtained in crystals containing 1 mol. alcohol.

α-γ-Dimethylbenzoylenecarbamide,  $C_6H_4\left<\begin{matrix}CO{-}NMe\\ |\\ NMe{\cdot}CO\end{matrix}\right.$, is obtained when benzoylenecarbamide is heated with alcoholic soda and methyl iodide (2 mols.) at 100°. It forms white needles which melt at 151°, sublime, and are unchanged by hydrochloric acid at 160—170°; it is soluble in alcohol, sparingly so in water.

γ-Methylbenzoylenecarbamide,  $C_6H_4\left<\begin{matrix}CO{\cdot}NMe\\ |\\ NH{\cdot}CO\end{matrix}\right.$, formed when orthamidobenzomethylamide is heated with carbamide at 200°, crystallises in long, hard, white needles, melts at 234°, and is unchanged by hydrochloric acid at 160—170°; it is sparingly soluble in water, but soluble in alcohol, and sublimes unchanged; its *sodium* salt crystallises in small laminæ, and if this is heated at 100° with methyl iodide in alcoholic solution, dimethylbenzoylenecarbamide is formed.

When orthomethylamidobenzamide is heated with carbamide, *α-methylbenzoylenecarbamide*,  $C_6H_4\left<\begin{matrix}CO{-}NH\\ |\\ NMe{\cdot}CO\end{matrix}\right.$, is obtained; it crystallises in white needles which begin to soften at 138—140°, melt at 147—148°, and sublime. It is soluble in alcohol, and can be converted into dimethylbenzoylenecarbamide by heating with alcoholic soda and methyl iodide.

By heating benzoylenecarbamide with phosphorus pentachloride (2 mols.) in a solution of phosphorus trichloride at 150—160°, *β-δ-dichloroquinazoline*,  $C_6H_4\left<\begin{matrix}CCl{:}N\\ N{:}CCl\end{matrix}\right>$, is formed; it sublimes in white needles melting at 115°, and can also be obtained by heating γ-methylbenzoylenecarbamide with phosphorus pentachloride; quinazoline was not obtained from it by treatment with hydriodic acid.

Dimethoxyquinazoline,  $C_6H_4\left<\begin{matrix}C(OMe){:}N\\ N{:}C(OMe)\end{matrix}\right>$, is obtained by heating the above dichloro-compound with sodium methoxide (2 mols.) at 100°; it forms snow-white needles, melting at 66°, soluble in alcohol and methyl alcohol, sparingly soluble in water. A. G. B.

Action of Hydroxylamine on Bromacetophenone. By H. STRASSMANN (*Ber.*, **22**, 419—422).—Brom- and dibrom-acetophenone both yield phenylglyoxime when heated with hydroxylamine (compare Schramm, Abstr., 1884, 51). Phenylglyoxime melts at 162°, is readily soluble in ammonia, and yields a yellow silver salt. To prepare this compound from bromacetophenone, the ketone (1 mol.), dissolved in alcohol, is boiled for 10 hours with an aqueous solution of hydroxylamine hydrochloride. The whole is poured into a large quantity of water, the solution extracted with ether, and the extract shaken with dilute soda; the alkaline solution is acidified, extracted with ether, and the residue obtained on evaporation spread on a porous plate and repeatedly washed with benzene. F. S. K.

The Sulphonic Acids of Meta- and Para-xylidine. By E. NÖLTING and O. KOHN (*Chem. Centr.*, 1889, 254, from *Bull. Soc. indust. Mulhouse*, **58**, 636—647).—Only one and the same sulphonic acid can be obtained from metaxylidine, however the conditions of the reaction be varied. It is sparingly soluble in water and dilute sulphuric acid, and when heated decomposes without melting. It is completely decomposed into xylidine and sulphuric acid by heating with hydrochloric acid at 180°. *Diazometaxylenesulphonic acid*, $C_8H_2Me_2N_2SO_3$, is prepared by treating sodium xylidinesulphonate with the calculated quantity of sodium nitrite and hydrochloric acid. It is a white, crystalline substance, sparingly soluble in water and very stable. It forms double salts with phenols and amines. *Bromoxylenesulphonic acid*, $C_6H_2Me_2Br{\cdot}SO_3H$, is obtained by treating the diazosulphonic acid with hydrobromic acid. The *sulphonamide*, $C_6H_2Me_2Br{\cdot}SO_2{\cdot}NH_2$, is obtained from its sodium salt by the action of phosphorus pentachloride.

The following derivatives of the paraxylidinesulphonic acid,

$$[C_6H_2Me_2(NH_2){\cdot}SO_3H = 1:4:2:5],$$

were prepared:—The *diazosulphonic acid* and *bromo-xylenesulphonic acid*, melting at 65°. *Paraxylidinesulphonic acid*, $C_6H_2Me_2(NH_2)SO_3H$ (1 : 4 : 2 : 6), is obtained from paraxylenesulphonic acid by conversion into the nitro-acid and subsequent reduction by ammonium hydrosulphide. Chromic acid does not oxidise it to a quinone. Bromoparaxylidinesulphonic acid is prepared in like manner to the meta-compound. J. W. L.

Two Isomeric Benzilemonoximes. By K. AUWERS and V. MEYER (*Ber.*, **22**, 537—551; compare this vol., p. 403).—α-Benzilemonoxime is best prepared by adding a concentrated aqueous solution of hydroxylamine hydrochloride (3½ parts) and soda (4 parts) to a cold alcoholic solution (30 parts) of benzile (10 parts). The mixture is kept for some hours at the ordinary temperature, then poured into water, the solution filtered and acidified. An oil separates at first, but solidifies after some time, and the crystalline product, which consists of a mixture of about equal quantities of α- and β-benzilemonoxime, is recrystallised from dilute alcohol or treated with a quantity of benzene insufficient to dissolve the whole. The α-compound being more sparingly soluble in both solvents separates from the alcohol or remains undissolved by the benzene, and is purified by repeatedly recrystallising from hot 30 per cent. alcohol. The β-oxime in the mother-liquors is purified by recrystallisation from benzene. Pure α-benzilemonoxime crystallises in nacreous, quadratic plates, melts at 137—138°, and is more sparingly soluble than the β-oxime (compare Wittenberg and Meyer, Abstr., 1883, 803; and Meyer and

Oelkers, Abstr., 1888, 703). The *acetyl*-derivative crystallises in broad, flat prisms, melts at 61—62°, and is readily soluble in most ordinary solvents except water; it is reconverted into the α-oxime when warmed with soda.

β-Benzilemonoxime is best prepared by digesting a moderately concentrated aqueous-alcoholic solution of benzile at 100° with rather less than the theoretical quantity of hydroxylamine hydrochloride. The product, which consists of the β-oxime alone, is purified by recrystallising it from benzene. The yield is almost theoretical. It crystallises from benzene with ½ mol. of benzene in compact prisms and needles melting at about 70°; the crystals effloresce on exposure to the air, and then melt at about 113—114°. It is very readily soluble in most ordinary solvents, but only sparingly in light petroleum, and almost insoluble in water. It separates from dilute alcohol in an oily condition, but gradually solidifies to a mass of colourless needles or compact crystals: the latter melt at 113°, the needles generally melt at 90—95°, but after recrystallising from benzene the melting point is raised to 113°. This lower melting modification, the formation of which has also been observed in preparing other monoximes, may be a third isomeride. *β-Acetylbenzilemonoxime* resembles the corresponding α-compound, but the crystals are more slender and melt at 78—79°; it is reconverted into the β-oxime when heated at 110° with soda.

Determinations of the molecular weights of α- and β-benzilemonoxime by Raoult's method in glacial acetic acid solution showed that the two compounds are isomeric.

α-Benzilemonoxime is completely converted into the β-compound when heated at 100° for a long time with absolute alcohol, or when kept for some time in a cold solution of glacial acetic acid and acetic anhydride saturated with hydrogen chloride.

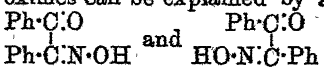
Both benzilemonoximes are decomposed when heated for a long time at 100° with concentrated hydrochloric acid, yielding benzile and hydroxylamine hydrochloride together with a small quantity of benzoic acid and ammonia.

When α-benzilemonoxime (1 part) is treated at the ordinary temperature with hydroxylamine hydrochloride (2 parts) and soda (4 parts) in aqueous solution, or with hydroxylamine hydrochloride (2 parts) alone in alcoholic solution, it yields α-benziledioxime together with small quantities of compounds of lower melting point.

β-Benzilemonoxime behaves in like manner when treated with hydroxylamine in aqueous solution, but traces of the α-dioxime are also formed, and in addition a third isomeride, which is entirely converted into the β-dioxime when heated for a long time at 140°.

Both monoximes combine with phenylhydrazine, yielding yellowish-red, amorphous compounds, and both are optically inactive.

These results show that the isomerism of the two benzilemonoximes can be explained by assuming that they have the constitution



$\begin{array}{l}\mathrm{Ph{\cdot}C{:}O}\\ \quad| \\ \mathrm{Ph{\cdot}C{:}N{\cdot}OH}\end{array}$ and $\begin{array}{l}\quad\mathrm{Ph{\cdot}C{:}O}\\ \qquad| \\ \mathrm{HO{\cdot}N{:}C{\cdot}Ph}\end{array}$ respectively. (Compare Beckmann, this vol., p. 608.)

The two modifications of benzophenone melting at 48—49° and

26—27° respectively yield one and the same benzophenonemonoxime (m. p. 140°) when treated with hydroxylamine in dilute alcoholic solution, either in the cold or at 100° ; the same oxime is formed, but much more slowly, when either modification of the ketone is treated under the same conditions with hydroxylamine hydrochloride. This oxime is not converted into an isomeric compound when heated with alcohol at 180°.

Benzophenone melting at 26—27° is most easily prepared by heating the isomeric compound (m. p. 48—49°) for a short time to its boiling point and then distilling. F. S. K.

Aldine Formation. By E. BRAUN (*Ber.*, **22**, 556—561 ; compare Braun and Meyer, Abstr., 1888, 1093).—When benzilemonoxime is reduced with stannous chloride and hydrochloric acid, a salt, probably $COPh{\cdot}CHPh{\cdot}NH_2,HCl$, melting at 207—209°, is obtained. The free *base*, as prepared by decomposing the hydrochloride with soda or ammonia, is a colourless, crystalline powder melting at 60—70°, and almost insoluble in water, but readily soluble in all other solvents. It is difficult to obtain it in crystals, but in one experiment it separated from ether in slender, moss-like forms melting at 105—109°. By direct comparison with the base $OH{\cdot}CHPh{\cdot}CHPh{\cdot}NH_2$, obtained by Goldschmidt and Polonowska (Abstr., 1888, 485) by reducing benzilemonoxime with sodium amalgam and acetic acid in alcoholic solution, and by studying the properties and salts of the two compounds, it was found that these two bases are not identical; the constitution of the new base is, therefore, most probably $COPh{\cdot}CHPh{\cdot}NH_2$.

Tetramethylaldine is obtained when isonitrosoacetophenone is reduced with stannous chloride and hydrochloric acid, the solution freed from tin and mixed with excess of alkali; if, however, after removing the tin, the solution is evaporated and the residue extracted with alcoholic ether to remove ammonium chloride, the *hydrochloride* of a new base remains. This salt is very hygroscopic but crystallises when kept in a partial vacuum. A compound, the composition of which is probably $(C_4NH_7Cl)_2PtCl_2$, separates in compact, dark-red crystals, when a concentrated, aqueous solution of the hydrochloride is mixed with platinic chloride and kept over sulphuric acid in a partial vacuum; it is readily soluble in water. F. S. K.

Aldine Formation. By E. GUDEMAN (*Ber.*, **22**, 562—564).—Isonitrosopropiophenone (compare v. Pechmann and Müller, Abstr., 1888, 1087) crystallises from hot water in long needles, melts at 114°, dissolves in alkalis with an intense yellow coloration, and distils without decomposition when heated in small quantities. The *oxime*, $NOH{:}CPh{\cdot}CMe{:}NOH$, crystallises in colourless needles, melts at 231—233°, and distils undecomposed when heated in small quantities. When isonitrosopropiophenone is treated with stannous chloride and hydrochloric acid, it yields acetylbenzoyl (compare v. Pechmann and Müller, *loc. cit.*), but when reduced with sodium amalgam in aqueous alkaline solution, it yields a yellow, oily base, $C_{18}H_{18}N_2O$. This compound is much more unstable than the base described by Braun and Meyer (Abstr., 1888, 1093); in the dry state it can be kept without change, but when treated with acids or alkalis it is converted into orange-red or colourless products. It dissolves in concentrated hydrochloric acid, forming a deep orange-red solution, but on diluting, a rose-red, neutral substance is precipitated, and the filtrate therefrom contains a base which is precipitated on adding sodium carbonate. This base crystallises from alcohol in small needles melting at 106—108°. F. S. K.

Fichtelite. By C. Hell (*Ber.*, **22**, 498—502).—Fichtelite occurs together with retene in the fossil stems of the sporadic marsh-fir (*Pinus uliginosa*, N. It was discovered by Trommsdorf (*Annalen*, **21**, 126), and has been investigated by Bromeis (*ibid.*, **37**, 304) and Clark (*ibid.*, **103**, 236). It is best obtained in the pure state by recrystallising from a mixture of alcohol and ether, from which it separates in long prisms melting at 46°; the mother-liquors, on further evaporation, yield retene and a brown, semi-fluid substance, which has a strong smell of vanilla. Vapour-density determinations made by Meyer's method at 440° with several samples of carefully purified fichtelite, seem to show that this hydrocarbon has the molecular formula $C_{15}H_{28}$ or $C_{15}H_{26}$; as, however, it is quite possible that partial decomposition may have occurred, the true molecular formula may be $C_{30}H_{54}$, which composition agrees best with the author's analyses, and also with those made by Clark (*loc. cit.*).

Fichtelite is only acted on extremely slowly by oxidising agents in aqueous solution, but when treated with a glacial acetic acid solution of chromic acid, it is completely oxidised to carbonic anhydride, or, possibly, to acetic acid. Cold nitric acid is without action, but when the hydrocarbon is boiled with nitric acid of sp. gr. 1·32, it yields oxalic acid and resinous nitrogenous substances, which disappear again on continued boiling. It is only acted on very slowly when heated with fuming sulphuric acid; it is, however, energetically attacked by bromine but no pure derivatives could be obtained.

F. S. K.

β-Chloro-α-bromonaphthalene. By J. Guareschi (*Chem. Centr.*, 1888, 1545; *Ann. Chim. Farm.*, **8**, 106—111).—40 grams of β-monochloronaphthalene, when treated with 13·5 c.c. bromine in the cold, gave a crystalline mass, from which a colourless substance, melting at 68—69°, and a colourless liquid were obtained.

The former is *β-chloro-α-bromonaphthalene.* It crystallises in colourless needles or plates, boils at 275—280° under 745 mm. pressure, and is soluble in alcohol and ether, insoluble in water. Boiling with chromic acid dissolved in glacial acetic acid oxidised it to β-monochlorphthalic acid; a little α-monobromphthalic acid was also formed.

J. W. L.

Naphthaquinonedichlorodiimide. By P. Friedländer and O. Böckmann (*Ber.*, **22**, 590—591).—*Naphthaquinonedichlorodiimide*, $C_{10}H_6(NCl)_2$, is obtained when 1, 4-naphthalenediamine is dissolved in excess of hydrochloric and treated in the cold with a solution of bleaching powder as long as a precipitate is produced. It crystallises from alcohol or xylene in bright yellow needles melting at

136—137°. It has an intense quinone-like odour, and behaves in all respects like a chloroquinoneimide. It is reconverted into the diamine by reducing agents, but when treated with cold concentrated hydrochloric acid in glacial acetic acid solution, it yields dichloro-α-naphthaquinone, melting at 190°. When warmed with sodium sulphite, it yields a naphthylenediamine or an amidonaphtholsulphonic acid, which crystallises in colourless sparingly soluble plates. It reacts energetically with primary and tertiary naphthalene and benzene bases, forming condensation-products which are generally brightly coloured. F. S. K.

Constitution of α-Hydroxynaphthoic Acid. By R. WOLFFENSTEIN (*Chem. Centr.*, 1889, 75—76).—Dichlororthophosphorylnaphthotrichloride, prepared from α-hydroxynaphthoic acid, does not react with anhydrous acetic acid and sodium acetate; by heating with anhydrous acetic acid alone, α-hydroxynaphthoic-phosphoric acid, and at a higher temperature α-hydroxynaphthoic acid are formed. When treated with absolute alcohol in the cold, the trichloride is converted into the *diethylorthophosphate* of *hydroxynaphthotrichloride*, $PO(OEt)_2 \cdot O \cdot C_{10}H_6 \cdot CCl_3$. This melts at 63°, and when heated with water α-hydroxynaphthoic acid is regenerated. If the trichloride is heated with alcohol, all the chlorine is eliminated, with formation of a difficultly crystallisable mass. Ammonia gas reacts with the trichloride, forming a compound containing nitrogen, phosphorus, and chlorine. When heated with phosphorus pentoxide, the trichloride is converted into *chlornaphthotrichloride*, $C_{10}H_6Cl \cdot CCl_3$, melting at 75°. If this is dissolved in anhydrous acetic acid, water added, and then boiled, α-chloro-β-naphthoic acid, $C_{10}H_6Cl \cdot COOH$, is formed, which is converted into β-naphthoic acid by reduction with sodium amalgam. From these reactions it is apparent that the hydroxyl-group in α-hydroxynaphthoic acid occupies the position 1. J. W. L.

Constitution of Filicic Acid. By E. PATERNÒ (*Ber.*, **22**, 463—465).—The author is of opinion that as yet nothing is known of the constitution of filicic acid (compare Daccomo, this vol., p. 54). This acid cannot be an isobutrylhydroxynaphthaquinone, as stated by Daccomo, because such a compound would have the composition $C_{14}H_{12}O_4$, and would be a neutral substance, whereas, according to Daccomo himself, it has the composition $C_{14}H_{16}O_5$. Granting that filicic acid has this constitution, it seems quite impossible that such a compound could be made to take up 6 atoms of hydrogen by such simple means as those employed by Daccomo. The compound $C_{14}H_{22}O_{11}$ could not possibly be obtained, and the analysis upon which this formula was based is utterly worthless, as Daccomo overlooked the fact that in the combustion of a barium salt a considerable portion of the carbon remains as barium carbonate. It seems also hardly possible that a hydroxyquinone-derivative should combine so readily with 4 mols. of phenylhydrazine. F. S. K.

Spontaneous Oxidation of Essential Oils. By G. PAPASOGLI (*Chem. Centr.*, 1888, 1548—1549, from *L'Orosi*, **11**, 289—299).—In a large flask a layer of oil of turpentine 5—6 cm. deep was placed on the surface of about 250 c.c. of water and exposed to sunlight. From the water, camphoric acid was extracted by shaking with ether; formic and acetic acids were also formed. and of course also hydrogen peroxide. By extracting the water, which had been in contact with turpentine, with soda, an acid isomeric with campholic acid is separated, melting at 125°. It is little soluble in cold water, somewhat soluble in hot water, ether, chloroform, benzene, and hot turpentine, very soluble in alcohol. Oxidised oil of turpentine reacts with sodium, with evolution of a gas, and, seemingly, the formation of hydroxysylvic acid. Oil of eucalyptus absorbs oxygen readily, with formation of carbonic anydride and hydrogen peroxide. Meat kept in the water containing the oxidation products of oil of turpentine for eight months remained quite good, and the same medium rendered putrid fish odourless. J. W. L.

Australene. By P. Barbier and J. Hilt (*Compt. rend.*, **108**, 519—520).—Australene, which was first described by Berthelot in 1854, is a colourless, very mobile liquid, with a faint odour different from that of lævogyrate terebenthene. Its sp. gr. at 0° = 0·8789; mean coefficient of expansion between 0° and 100°, 0·0010425; refractive index for D = 1·4689 at 18·7°; specific refractive energy = 0·5440; rotatory power, $[\alpha]_D = +22·85°$.

When heated at 300° for two hours, australene is converted into *iso-australene*, which undergoes no further alteration at 300°. Isoaustralene is a colourless, mobile liquid, with a faint orange-like odour. It boils at 177·5; sp. gr. at 0° = 0·8593; mean coefficient of expansion between 0° and 100° = 0·001017; refractive index for D = 1·4749 at 17°; specific refractive energy = 0·5626. The rotatory power is opposite in sign to that of australene, and is greater the lower that of the australene from which it was formed. The boiling points and rotatory powers of two samples of australene before and after heating at 300° were as follows:—

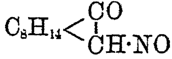
	Before.		After.	
	Boiling point.	Rotatory power.	Boiling point.	Rotatory power.
A	157—159°	+20·33°	177°	−16·16°
B	159—161	+13·08	177	−18·72

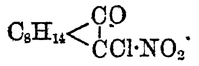
C. H. B.

Oil of Myrtle. By E. Jahns (*Arch. Pharm.* [3], **27**, 174—177).—The sample of oil of myrtle examined was of Spanish origin; its sp. gr. was 0·910 at 16°, and its rotatory power was $[\alpha]_D = +26·7°$. On fractional distillation, the terpene, $C_{10}H_{16}$, came over at 158—160°; its rotatory power $[\alpha]_D = +36·8°$; from its chemical properties it corresponds with dextropinene.

Cineole, boiling at 170°, a second constituent, could not be rectified by repeated distillation over sodium. The fraction passing over at 175—178° was therefore treated by Wallach's process, namely, hydrogen chloride was passed through the ice-cold liquid, the crystals obtained were pressed and decomposed by the addition of water, the separated oil warmed with dilute potassium hydroxide, washed with water, dried and rectified over sodium. The product showed all the characteristics of cineole. Besides these two main constituents a little camphor was present, but could not be isolated.

J. T.

Nitro-camphor. By P. CAZENEUVE (*Compt. rend.*, 108, 243—245).—The author has previously described the salts of nitrocamphor. If Kekulé's formula for camphor is accepted, nitrocamphor will have the constitution  $C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CH\cdot NO_2}$, and the chloro-nitro-derivative, which is a neutral compound, will have the constitution

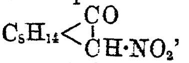
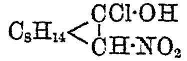
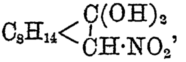
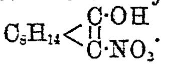


$$C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CCl\cdot NO_2}.$$

The existence of a ketonic function has not previously been established. When a neutral solution of the sodium salt is boiled with phenylhydrazine, it yields a yellow precipitate, which can be crystallised from boiling alcohol and has the composition $C_{10}H_{22}N_2$. It is therefore identical in composition with the substance formed by the action of phenylhydrazine on ordinary camphor. Its solubility in cold alcohol makes it easy to separate it from the other products of the reaction.

50 grams of nitro-camphor, 20 c.c. of absolute alcohol, and 3 c.c. of hydrochloric acid are boiled together for two or three minutes, cooled, and mixed with 2 vols. of water. The product soon solidifies to a crystalline mass, which is washed with cold alcohol of 63°, and recrystallised from benzene, since it is partially decomposed by alcohol. The product has the composition $NO_2\cdot C_{10}H_{15}O,HCl$, melts at 127—128°, is insoluble in water, undergoes double decomposition with silver nitrate, and has no action on ferric chloride. If, however, it is heated with alcohol of 60°, dilute hydrochloric or nitric acid and ferric chloride, it yields a fine violet colour. Under the influence of acids and dilute alcohol, it yields a hydrate which, however, cannot be isolated. This hydrate is also obtained by heating 5 grams of nitrocamphor with 60 c.c. of alcohol of 93°, and 5 c.c. of hydrochloric acid for 15 minutes. The product is saturated with barium carbonate, filtered, mixed with 4 vols. of water to precipitate resinous matter, and again filtered and evaporated in a vacuum. The small crystals which separate are heated with 10 to 15 times their volume of water until melted, then mixed with sufficient alcohol of 93° to dissolve the melted crystals, and the solution is allowed to cool, when it deposits long, acicular crystals. The compound itself has the empirical formula of a hydrate of nitrocamphor, but the composition of the barium salt, $(NO_2\cdot C_{10}H_{14}O)_3BaH + 3H_2O$, shows that it is trihydric, and that polymerisation has taken place. This salt melts at 75°, loses 3 mols. H_2O over sulphuric acid in a vacuum, and then melts at 98°. The free substance has all the characters of a phenol. It is neutral to litmus, does not decompose carbonates, combines with bases, and is not reduced by phenylhydrazine. With acetic chloride it splits up and yields an ethereal salt; with ferric chloride it gives a blood-red colour. In presence of dilute acid this coloration becomes violet and

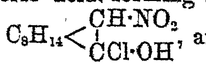
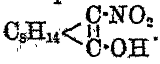
is altered by boiling. The substance giving the latter reaction is, however, only stable in aqueous solution in presence of dilute acids.

Nitrocamphor,  $C_8H_{14}<\begin{matrix}CO\\ |\\ CH\cdot NO_2\end{matrix}$, forms a hydrochloride which changes into  $C_8H_{14}<\begin{matrix}CCl\cdot OH\\ |\\ CH\cdot NO_2\end{matrix}$ and then into  $C_8H_{14}<\begin{matrix}C(OH)_2\\ |\\ CH\cdot NO_2\end{matrix}$, and the latter polymerises and becomes $(C_{10}H_{17}NO_3)_3,3H_2O$, which eventually changes into a very stable compound which will shortly be described,  $C_8H_{14}<\begin{matrix}C\cdot OH\\ \|\\ C\cdot NO_2\end{matrix}$. Nitrocamphor is a ketone rather than an aldehyde, and the aldol reaction is due to the presence of hydrogen in the $CH\cdot NO_2$ group which is in direct union with the CO group.

C. H. B.

A Nitrophenol Isomeric with α-Nitrocamphor. By P. Cazeneuve (*Compt. rend.*, **108**, 302—304; compare preceding Abstract).—α-Nitrocamphor is boiled for half an hour with 10 times its weight of concentrated hydrochloric acid. Nine-tenths of it dissolves and the solution is diluted with three volumes of water, agitated with animal charcoal, filtered, evaporated to dryness, and the product recrystallised from hot water. It has the composition $C_{10}H_{15}NO_3$, and crystallises in long needles which contain 1 mol. H_2O. From dilute alcoholic solution it separates in modified rhombic prisms, the dominant form being *mpe′g′*. The hydrated crystals soften at 60° and melt at 70°; the anhydrous substance melts at 220°, with partial decomposition. Water dissolves 7 per cent. of the substance at 15° and an unlimited quantity at 100°. It is also soluble in alcohol, ether, chloroform, and benzene. It is dextrogyrate, and the rotatory power of a 1·8 per cent. solution in alcohol is $[\alpha]_D = +10°$. It reddens litmus, decomposes carbonates, and combines with metals to form salts which, as a rule, are soluble in water. The mercuric and silver salts are only slightly soluble, the barium and calcium salts are almost insoluble, the quinine and cinchonine salts are insoluble, but the morphine and strychnine salts are somewhat soluble. Phenylhydrazine has no reducing action on the compound, and this indicates that the ketonic function has been removed.

Acetic chloride yields an acetyl-derivative isomeric with acetyl nitrocamphor. It separates from an alcoholic solution in hard, white crystals, which melt at 115° without decomposition. It is dextrogyrate, the rotatory power of a 2 per cent. solution in alcohol being $[\alpha]_D = +4° 25'$; it boils at 150—200°, and at the same time decomposes and gives off hydrogen chloride. It has a neutral reaction, gives no coloration with ferric chloride, and is decomposed by alcoholic potash with formation of potassium acetate.

It has previously been shown (*loc. cit.*) that α-nitrocamphor combines with hydrochloric acid, forming a compound which probably has the constitution  $C_8H_{14}<\begin{matrix}CH\cdot NO_2\\ |\\ CCl\cdot OH\end{matrix}$, and hence it would seem that the phenolic compound now described must have the constitution  $C_8H_{14}<\begin{matrix}C\cdot NO_2\\ \|\\ C\cdot OH\end{matrix}$.

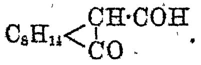
C. H. B.

Nitrosocamphor and Camphorquinone. By L. Claisen and O. Manasse (*Ber.*, 22, 530—533).—*Nitrosocamphor* can be prepared by adding a well-cooled solution of camphor (152 grams) in amyl nitrite (117 grams) and ether (50 c.c.) to powdered sodium ethoxide (70 grams) suspended in ether (about 75 c.c.). The mixture is shaken well and kept at the lowest possible temperature for some time, then the sodonitrosocamphor is extracted with cold water, the solution shaken with ether, and the nitroso-derivative precipitated with acetic acid. About 55 grams of the nitroso-compound is generally obtained. It is readily soluble in amyl alcohol, ethyl alcohol, ether, and chloroform, but more sparingly in benzene, and almost insoluble in light petroleum; it crystallises from benzene, dilute alcohol or water, and melts at 153—154°.

Camphororthoquinone, $C_8H_{14}<\begin{matrix}CO\\ |\\ CO\end{matrix}$, is formed, with evolution of nitrous oxide, when a concentrated aqueous solution of sodium nitrite (1 to 1½ mols.) is gradually added to a glacial acetic acid solution of nitrosocamphor; on diluting with water, the product is precipitated in yellow crystals. The yield is from 60 to 75 per cent. of the theoretical. It can also be obtained by dissolving nitrosocamphor in a large quantity of hydrogen sodium sulphite solution and boiling the filtered solution with excess of dilute sulphuric acid. The yield is about 10 to 20 per cent. less than by the first method. It crystallises from alcohol or water, melts at 198°, sublimes at 50—60° in golden-yellow needles, and is volatile with steam. It is readily soluble in ether, hot alcohol, and boiling water, but only sparingly in the cold: the hot, aqueous solution has a peculiar, sweet smell. In physical properties, this compound bears some resemblance both to 1 . 2 diketones and to aromatic quinones. F. S. K.

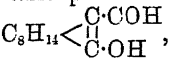
Camphoraldehyde. By A. W. Bishop and L. Claisen (*Ber.*, 22, 533—537).—*Camphoraldehyde*, $C_{11}H_{16}O_2$, is formed when camphor is treated with sodium and ethyl formate (compare Claisen and Lowman, Abstr., 1888, 692). The product is extracted with alkali, the solution shaken with ether to remove impurities, acidified with acetic acid, and the ketoaldehyde extracted with ether. It is a crystalline substance melting at 76—78°, and is a moderately strong acid, dissolving freely in alkalis, but not quite so readily in alkaline carbonates. The *copper* salt, $(C_{11}H_{15}O_2)_2Cu$, prepared by treating the ketoaldehyde with a solution of copper acetate, is a light-green, crystalline substance, sparingly soluble in water, but readily in all organic solvents. The *zinc* salt is colourless and has similar properties. Ferric chloride produces a dark-violet coloration in alcoholic solutions of the aldehyde. The *anilide*, $C_{17}H_{21}ON$, formed by treating the aldehyde with aniline at the ordinary temperature, is a colourless, crystalline compound, melting at 153°.

Camphoraldehyde most probably has the constitution



$$C_8H_{14}<\begin{matrix}CH\cdot COH\\ |\\ CO\end{matrix}.$$

Intramolecular change may, however, take place with formation of the possibly more stable compound,



$C_8H_{14}<\begin{matrix}C\cdot COH\\ \Vert\\ C\cdot OH\end{matrix}$

, in which case its constitution would be exactly analogous to that of salicaldehyde.

F. S. K.

Normal and Acid Ethereal Salts of Camphols. By A. Haller (*Compt. rend.*, 108, 410—412).

—The normal and acid succinates were obtained by heating borneol and succinic acid in the proper proportions at 130° for several days. The product was treated with ether, the ethereal solution agitated with an aqueous solution of sodium carbonate to remove the acid salt, the liquids separated, the ether distilled off, and the residue heated to expel excess of borneol. The crude product was recrystallised from alcohol. In order to obtain the acid salt, the solution of alkaline carbonate used for washing the crude product was acidified with sulphuric acid and the acid camphol succinate extracted with ether.

Both the normal and acid salts form white, acicular or prismatic crystals, very soluble in benzene, light petroleum, ethyl acetate, and ether, but less soluble in ethyl or methyl alcohols. The acid salts dissolve in solutions of sodium or potassium carbonate, but these solutions decompose on boiling, with formation of borneol and an alkaline succinate.

	Melting point.	Rotatory power.
Normal succinate of dextrogyrate camphol	83·7°	$[\alpha]_D = +42·05°$
Normal succinate of lævogyrate camphol	83·7	„ $= -42·09$
Normal succinate of racemic camphol	82·28	0
Acid succinate of dextrogyrate camphol	58·0	„ $= +35·59$
Acid succinate of lævogyrate camphol	50·0	„ $= -35·94$
Acid succinate of racemic camphol	56·5	0

The melting points of the salts of racemic camphol are very close to those of the active varieties. The borneol liberated from these salts has the same rotatory power as the original borneol.

The author also prepared the normal and acid succinates of an artificial camphol, which had a rotatory power of $[\alpha]_D = +10°$, and was a mixture of stable dextrogyrate and unstable lævogyrate camphol. The salts were separated by fractional crystallisation, and the four fractions gave the following results:—

	1.	2.	3.	4.
Melting point......	73·47°	67·37°	67·33°	60·32°
Rotatory power $[\alpha]_D$	+13·50	+6·84	+3·93	+8·20*

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* This seems to be a misprint for +3·20.

The melting point of the acid succinate was 41·5°, and its rotatory power +10·76°. C. H. B.

Phthalates of Camphols. By A. Haller (*Compt. rend.*, **108**, 456—457).—These ethereal salts were obtained in the same manner as the succinates (preceding Abstract). The normal dextrogyrate and lævogyrate phthalates crystallise in white needles, readily soluble in ether, benzene, ethyl acetate, light petroleum, and methyl and ethyl alcohols. The normal racemic phthalate crystallises in small, radiating prisms. The active acid phthalates form tabular or prismatic crystals, soluble in methyl or ethyl alcohol, ether, benzene, and alkalis. If the alkaline solutions are boiled, sodium phthalate and borneol are produced; the acid racemic phthalate forms stellate groups of needles, different in appearance from the active salts: it is soluble in ethyl and methyl alcohols and benzene.

	Melting point.	Rotatory power.
Normal dextrogyrate phthalate ..	101·12°	$[\alpha]_D$ = +79·54°
„ lævogyrate „ ..	101·12	„ = −79·14
„ racemic „ ..	118·00	„ = 0
Acid dextrogyrate „ ..	164·48	„ = +58·38
„ lævogyrate „ ..	164·48	„ = −58·27
„ racemic „ ..	158·34	„ = 0

It is noteworthy that there is a greater difference between the melting points of the active and inactive varieties than was observed in the case of the succinates, and that whereas the melting point of the normal racemic salt is higher than that of the normal active salts, the reverse is the case with the acid salts. C. H. B.

Dammara Resin. By B. Graf (*Arch. Pharm.* [3], **27**, 97—111).—Five East Indian varieties of dammara resin were examined, and were found to be tolerably uniform in composition. In opposition to previous observers, the resin was found to contain only about 1 per cent. of an acid, which proved to be bibasic and of the formula $C_{18}H_{33}O_3$ The other constituents, of which 40 per cent. was insoluble and 60 per cent. soluble in alcohol, appeared to be of no very pronounced chemical character, and in particular had no acid properties. The soluble portion has probably the molecular formula $C_{20}H_{42}O_2$, and melts at 61°. The presence of a pure hydrocarbon in dammara resin is denied. The portion insoluble in alcohol is not free from oxygen, and melts at 144—145°. J. T.

Artificial Diastase. By A. Reychler (*Ber.*, **22**, 414—419).—When freshly prepared wheat gluten is digested at 30—40° for a few hours with very dilute acids, considerable quantities of albuminoïds are dissolved, forming an opalescent solution. The acids or acid salts employed were hydrochloric acid, hydrogen potassium sulphite, phosphoric acid, alkaline dihydrogen phosphates, acetic acid, formic acid, tartaric acid, and lactic acid.

This opalescent solution is not coagulated by boiling; it gives a precipitate with a few drops of very dilute potash, soluble in excess. It becomes clear on adding two volumes of alcohol, but a turbidity is generally produced when the alcohol is added in large quantities. It gives a precipitate with potassium ferrocyanide, soluble in a large quantity of acetic acid. Mercuric chloride seems to produce no precipitate.

Tincture of guaiacum and hydrogen peroxide produce an intense blue coloration, but not if the solution has been previously boiled or treated with too much acid. A solution of the gluten from wheat flour (10 grams) in acetic acid ($\frac{1}{10000}$ 50 c.c.), gives this reaction most distinctly. This behaviour, according to Lintner, is characteristic of diastase.

The gluten solutions have a fermentive action similar to that of diastase, but they lose this property partially or completely when boiled, or in presence of alkalis or of too much acid. The gluten from 20 grams of wheat flour was digested for a few hours with 100 c.c. of an aqueous solution (500 c.c.) of potassium dihydrogen phosphate (1 gram). 2 c.c. of the solution were then added to starch (2 grams, 88 per cent.) made into a paste with water (250 c.c.), and the mixture kept for five hours at 40—50°. The solution thus obtained reduced 135 c.c. of Soxhlet's alkaline copper solution.

The soluble albuminoïds present in wheat flour also contain diastase, as can be proved by Lintner's reaction. Starch (4 grams) made into a paste with water was digested for two hours at 60—66°: (1) with an aqueous extract from 1·6 grams of wheat flour, and (2) with a similar extract to which 2 c.c. of hydrochloric acid ($\frac{1}{1000}$) had been added. At the end of this time the solutions still contained unchanged starch, and reduced 100 c.c. and 210 c.c. of Soxhlet's solution respectively, showing that a trace of acid increases the rapidity of fermentation.

The diastase-like action of the soluble albuminoïds in ungerminated barley can also be proved experimentally, and the author gives a table showing the reducing power of the solutions obtained when ungerminated barley (2 samples), maize, and malt, respectively, mixed either with water alone or with water and a trace of acetic or metaphosphoric acid, are kept at a suitable temperature. Under the above conditions, the starch in the grain is only slowly acted on; it was found that fermentation takes place much more rapidly when starch-paste is treated with a relatively small quantity of ungerminated barley. The results of experiments in this direction, in presence or in absence of a trace of acetic acid, are also given in a table.

The author considers that it is not improbable that in the germination of barley and other seeds, the solubility and fermentive power of a portion of the albuminoïds is produced by reactions similar to those which occur when gluten is dissolved in very dilute acids.

F. S. K.

Phycoerythrin. By F. Schütt (*Chem. Centr.*, 1889, 21, from *Ber. deut. bot. Gesell.*, 6, 305—323).—The light which causes the fluorescence of solutions of phycoerythrin consists essentially of rays of wave-lengths λ 590—560. Solutions of this dye are bleached by both light and air, although the action is a very slow one; heating to 60° bleaches them completely. Phycoerythrin is insoluble in all liquids which dissolve chlorophyll. It could not be split up into more than one substance by fractional crystallisation, but the substance as precipitated by alcohol differs so much from the original that the author has designated it *β-phycoerythrin.* A third modification, obtained by precipitating the dye from its solution with an acid, has been termed *γ-phycoerythrin.* Ammonia appears to precipitate the same modification as alcohol does. Fixed alkalis discharge the colour of the dye from its solutions. J. W. L.

Bidesyls. By H. C. FEHRLIN (*Ber.*, **22**, 553—556).—Bidesyl, melting at 254—255° (compare Knoevenagel, Abstr., 1888, 706), is converted into the isomeride (m. p. 260—261°) when boiled for two hours with a large quantity of alcohol. Both compounds dissolve in concentrated sulphuric acid with a grass-green coloration which gradually darkens, and finally becomes brown.

Acetyltetraphenylpyrroline, prepared by heating tetraphenylpyrroline (compare Garrett, this vol., p. 162) at 180—190° with acetic anhydride and sodium acetate, crystallises from glacial acetic acid or benzene in slender, colourless needles, melts at 226°, and is almost insoluble in alcohol.

Tetranitrotetraphenylpyrroline, $C_4NH(C_6H_4·NO_2)_4$, prepared by treating the pyrroline with fuming nitric acid, crystallises from glacial acetic acid in small, light yellow needles which decompose at 123°, but have no well-defined melting point. It is sparingly soluble in alcohol, and dissolves in warm, concentrated sulphuric acid, yielding a yellow solution which passes through green, and becomes violet-red.

Ethyltetraphenylpyrroline is obtained when a mixture of the two bidesyls is heated at 150° with a 33 per cent. solution of ethylamine. It crystallises from chloroform or benzene in small, slender needles, and from glacial acetic acid in small plates melting at 221°.

Methyltetraphenylpyrroline, prepared in like manner, crystallises from ether in small, feathery needles or plates, melts at 214°, and is readily soluble in hot alcohol, chloroform, and ether, and in cold benzene. F. S. K.

β-Methyl Pyridyl Ketone. By C. ENGLER and W. KIBY (*Ber.*, **22**, 597—599).—*Methyl pyridyl ketone*, $C_5NH_4·COMe$, is formed when an intimate mixture of calcium nicotinate (about 3 mols.), or an acid salt of quinolinic acid, and calcium acetate (4 mols.) is distilled in quantities of about 50 grams. The pyridine in the product is removed by distilling with steam, the residue is dissolved in hydrochloric acid, mixed with excess of soda, the solution separated from impurities, and extracted with ether. The oil, which is obtained on evaporating the ether, is fractionated, the portion passing between 200—260° treated with phenylhydrazine, and the resulting crystalline hydrazone decomposed with concentrated hydrochloric acid. The phenylhydrazine salt is separated, the solution treated with sodium nitrite, made strongly alkaline, and the ketone extracted with ether. It is a colourless oil, boils at 220°, and rapidly becomes yellow. It is readily soluble in all acids. The *hydrochloride* is very readily soluble, and cannot be obtained in crystals, but the *platinochloride* is crystalline. The *oxalate* crystallises from water and alcohol; the *picrate* crystallises from water in slender needles. The *mercurochloride* crystallises from hot water in white needles melting at 158°. The *hydrazone*, $C_{13}H_{13}N_3$, crystallises in yellow needles melting at 137°. The *oxime* is crystalline, and melts at 112°; its *hydrochloride*, $C_7H_8N_2O,HCl$, crystallises from alcohol, and melts at 204°.

F. S. K.

Condensation-products of Amidoacetal. By A. Wohl and W. Marckwald (*Ber.*, **22**, 568—580; compare A. Wohl, Abstr., 1888, 443, and Wolff, *ibid.*, 809).—Amidoacetal hydrochloride can be easily obtained in crystals by carefully neutralising an aqueous solution of the base with hydrochloric acid, and evaporating on the water-bath. The *picrate* crystallises in small, yellow, sparingly soluble needles, and melts at 142—143°.

Acetalylphenylthiocarbamide, $NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH(OEt)_2$, prepared by mixing equal parts of phenyl isothiocyanate and amidoacetal, crystallises from dilute alcohol in colourless needles, melts at 96°, and is readily soluble in ether, benzene, chloroform, and hot alcohol, but insoluble in water and light petroleum.

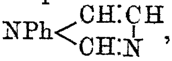
Phenylimidazolylmercaptide, $NPh<\begin{matrix}CH{=}CH\\ C(SH){:}N\end{matrix}>$, is formed when the preceding compound is boiled for half an hour with five times its weight of 30 per cent. sulphuric acid. It crystallises from hot water in long, colourless needles, melts at 181°, and is moderately soluble in hot alcohol, but only sparingly in the cold in most of the ordinary solvents. It has acid properties, and dissolves readily in dilute alkalis, but is insoluble in ammonia. Mercuric nitrate and stannous chloride produce a white, copper sulphate a dirty green and lead acetate a yellow precipitate in the aqueous solution. The *silver-derivative*, $C_9H_7N_2SAg$, is yellowish. These metallic compounds are decomposed by concentrated sulphuric acid with evolution of sulphurous anhydride. The compound, $(C_9H_8N_2S)_2PtCl_4$, prepared by treating an alcoholic solution of the mercaptide with platinic chloride, is a deep-red, crystalline substance.

The *methyl*-derivative, $C_{10}H_{10}N_2S$, is obtained when the mercaptide is treated with soda and methyl iodide in alcoholic solution. It is precipitated in slender, colourless needles, melting at 54° on adding water to the alcoholic solution, and it is very readily soluble in most ordinary solvents but insoluble in water. It dissolves freely in acids, but is reprecipitated by alkalis. The *nitrate* is very sparingly soluble in cold water, and separates from the hot solution in slender, colourless needles. The *platinochloride* and the *aurochloride* are amorphous. The *picrate*, $C_{10}H_{10}N_2S,C_6H_3N_3O_7$, crystallises from hot alcohol in yellow needles, and is sparingly soluble in water and alcohol. The methyl-derivative combines directly with methyl iodide, yielding a compound, $C_{11}H_{13}N_2SI$, which crystallises in colourless needles, melts at 177°, and is readily soluble in hot water and alcohol;

when boiled with moderately concentrated alkalis, it yields mercaptan.

The *sulphone*, $C_9H_7N_2{\cdot}SO_2Me$, prepared by oxidising the methyl-derivative with excess of warm, dilute nitric acid, crystallises from hot, dilute alcohol in small, slender, yellow needles, melts at 115—116°, and is readily soluble in most ordinary solvents, but only sparingly in water.

The *additive* compound, $C_{10}H_{11}N_2SI$, is formed when a cold, alcoholic solution of the mercaptide is treated with methyl iodide. It crystallises in colourless needles, melts at 152°, and yields the methyl-derivative when decomposed with alkalis.

Phenylimidazole,  $NPh<\begin{matrix}CH{:}CH\\ \qquad | \\ CH{:}N\end{matrix}$, is obtained when the mercaptide is digested with moderately dilute nitric acid, and the resulting salt decomposed with alkali. It is a colourless oil, boils at 276° (uncorr.), and mixes with most of the ordinary solvents, but is insoluble in water. The *picrate* crystallises in yellow needles, melts at 152°, and is sparingly soluble in water and cold alcohol. The *platinochloride*, $(C_9H_8N_2)_2,H_2PtCl_6$, crystallises from hot water in small, reddish-yellow plates, softens at 201—202°, and melts at a slightly higher temperature with evolution of gas. The *aurochloride*, $C_9H_8N_2,HAuCl_4$, forms pale-yellow crystals, and is soluble in hot water. Phenylimidazole combines with methyl iodide, yielding a syrupy additive compound which is readily soluble in water, and is not decomposed by concentrated alkalis.

The *compound* $NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CH(OH){\cdot}OEt$ separates in an oily condition when finely divided acetalylphenylthiocarbamide is dissolved in well-cooled, concentrated sulphuric acid, the solution poured into water, and mixed with excess of alkali. It crystallises from hot, dilute alcohol in colourless needles, melts at 94°, and is sparingly soluble in water but readily in alcohol, ether, and most ordinary solvents. Aqueous solutions are precipitated by argentic and mercuric nitrate. When heated at 100° with hydrochloric acid, or when boiled with 30 per cent. sulphuric acid, it is converted into phenylimidazole (see above). It combines with acids, yielding salts of a base, $C_{11}H_{14}N_2SO$. The *platinochloride*, $(C_{11}H_{14}N_2SO)_2,H_2PtCl_6$, is a yellow, crystalline compound. The *picrate*, $C_{11}H_{14}N_2SO,C_6H_3N_3O_7$, crystallises in small, yellow needles, melts at 190° with decomposition, and is moderately soluble in hot alcohol but only sparingly in water and cold alcohol. F. S. K.

Codeïne. By A. Knoll (*Arch. Pharm.* [3], **27**, 229, from *Pharm. Centrh.*, **30**, 39).—Some years back codeïne was prepared synthetically from morphine by substituting a methoxyl-group for a hydroxyl-group. In place of methyl chloride, Knoll proposes the use of a methyl-sulphate for this purpose. The mass is taken up with dilute sulphuric acid, and the codeïne is separated from a residue of undecomposed morphine by treatment with ammonia, when, on diluting somewhat, the codeïne remains in solution. The codeïne thus obtained is chemically pure, and agrees completely in all its properties with natural codeïne obtained from opium. J. T.

Constitution of the Cinchona Alkaloïds: Quinine. By Z. H. Skraup (*Monatsh.*, **10**, 39—50; compare Abstr., 1887, 164).—On careful oxidation with potassium permanganate, quinine, like cinchonine, furnishes a base of the composition $C_{19}H_{22}N_2O_4$. It melts with decomposition between 240° and 286°, and does not react with phenylhydrazine; when treated with acetic chloride it gives a base the platinochloride of which is an insoluble, yellowish-red powder of the formula $C_{19}H_{21}AcN_2O_4,H_2PtCl_6$, and on heating at 100° for 19 hours with 15 times its weight of a saturated solution of hydrobromic acid, it forms a salt, $C_{19}H_{22}N_2O_4 2HBr$, crystallising in white needles containing 1 or 1½ mols. of water. This base appears to be identical with *chitenine* obtained from cinchonine, for on oxidation with chromic acid it furnishes a mixture of quinic, α-pyridinetricarboxylic (α-carbocinchomeronic), and cincholeuponic acids. The last-named acid when anhydrous melts at 225—226°, when crystallised with 1 mol. of H_2O, at 126—127°. The hydrochloride, $C_8H_{13}NO_4,HCl$, melts with decomposition at 193—194°, and has the same rotatory power as the hydrochloride of the acid obtained similarly from cinchonidine, with which it must be identical. It may, therefore, be concluded that one-half of the quinine molecule has the same constitution as one-half of the cinchonine molecule, quinine being a derivative of paramethoxyquinoline, and cinchonine a derivative of quinoline. G. T. M.

Constitution of the Cinchona Alkaloïds: Cinchonidine. By H. Schniderschitsch (*Monatsh.*, **10**, 51—64; compare preceding Abstract).—Cinchonine and cinchonidine both give cincholeuponic acid when oxidised with potassium permanganate, and both contain 1 atom of hydrogen, replaceable by an acid radicle. The author suggests that the isomerism of the compounds must be that known as "physical," or that a slight difference exists in the mode of attachment of the piperidine- and quinoline-groups which both may be considered to contain. G. T. M.

Constitution of the Cinchona Alkaloïds: Quinidine. By J. Würstl (*Monatsh.*, **10**, 65—72; compare preceding Abstracts).—The difference in constitution between quinine and quinidine appears to be of the same nature as that existing between cinchonine and cinchonidine, for both alkaloïds give quinic and cincholeuponic acids on oxidation with potassium permanganate, and both contain one hydrogen-atom replaceable by acid radicles. G. T. M.

Strychnine. By K. v. Garzarolli-Thurnlackh (*Monatsh.*, **10**, 1—8).—*Strychnine benzyl chloride*, $C_{21}H_{22}N_2O_2,C_7H_7Cl + H_2O$, is obtained by heating together strychnine and benzyl chloride. It crystallises from hot water in short, thick prisms or in lustrous plates, melts at 262—263° with complete decomposition, and has a strong toxicological action. From the chloride, the following compounds can be readily prepared:—The *nitrate*, $C_{21}H_{22}N_2O_2,C_7H_7NO_3$, crystallises in lustrous prisms or in scales, and decomposes at 262—265° with partial fusion; the *dichromate*, $(C_{21}H_{22}N_2O_2,C_7H_7)_2Cr_2O_7$, is only slightly soluble in water, and crystallises in minute prisms; the *thio-*

cyanate, $C_{21}H_{22}N_2O_2,C_7H_7CNS$, crystallises in interlaced groups of needles melting at 236—237°; the *platinochloride*,

$$(C_{21}H_{22}N_2O_2,C_7H_7)_2PtCl_6,$$

melts at 215—216°; the *hydroxide*, $C_{21}H_{22}N_2O_2,C_7H_7{\cdot}OH$, crystallises in silky, red needles, and is a strongly alkaline base.

When strychnine benzyl chloride is oxidised with potassium permanganate, benzoic acid is the chief product, a brown resinous substance being produced at the same time. G. T. M.

Hydrastine. By M. FREUND (*Ber.*, 22, 456—459; compare Freund and Will, Abstr., 1887, 1057, and Roser, this vol., p. 417).—When hydrastinine is oxidised in dilute alkaline solution with a cold saturated solution of potassium permanganate, it is converted into oxyhydrastinine. The yield is almost quantitative.

The decomposition of hydrastinine under the influence of alkalis (*loc. cit.*), the oxidation of hydrohydrastinine to hydrastinine, and the conversion of the latter into oxyhydrastinine, show that these compounds stand in the same relation as alcohol, aldehyde, and acid.

The *oxime hydrochloride*, $C_{11}H_{14}N_2O_3,HCl$, separates in crystals when an alcoholic solution (20 c.c.) of hydrastinine (1 gram) is boiled for a few minutes with hydroxylamine hydrochloride, and then allowed to cool. It is readily soluble in water, and on adding ammonia or sodium carbonate solution, the free base is precipitated. The *base*, $C_{11}H_{14}N_2O_3$, crystallises from alcohol in colourless needles, melts at 145—146°, and is soluble in alkalis. The *platinochloride*, $C_{11}H_{14}N_2O_3,H_2PtCl_6$, is crystalline.

The *periodide*, $C_{11}H_{11}NO_2I_2,HI$, is precipitated when a solution of hydrastinine hydrochloride is treated with a solution of iodine in potassium iodide, or boiled for a few minutes with concentrated hydriodic acid. It crystallises from dilute alcohol in brown needles, melts at 132—134°, and is sparingly soluble in hot water. When an aqueous solution of hydrohydrastinine hydrobromide is exposed to the vapour of bromine, a red substance separates, and is obtained in colourless needles, melting at about 280°, by washing with boiling alcohol, and recrystallising several times from hot water. If a solution of this substance is treated with alkalis and the precipitate recrystallised from alcohol, the compound $C_{11}H_9Br_2NO_2$ separates in colourless needles melting at 125°.

The neutral substance occurring in *Hydrastis canadensis* (compare Freund and Will, Abstr., 1887, 174) is meconine, and the compound (m. p. 158°) obtained therefrom by the action of nitric acid is nitromeconine. F. S. K.

Berberine. By P. MARFORI (*Chem. Centr.*, 1888, 1620—1621, from *Ann. Chim. Farm.*, 8, 153—164).—Berberine reacts with nitric acid of sp. gr. 1·23 at 60°, or sp. gr. 1·16 at 75°, with formation of a golden-yellow, crystalline substance, *berberinic acid*, $C_{16}H_{13}NO_6$. It decomposes at 210°, is little soluble in water, very slightly soluble in hydrochloric acid. With Fröhde's reagent, it gives a blood-red coloration. The silver salt is a yellowish precipitate.

From the mother-liquor, water precipitates a yellowish substance, soluble in alcohol and water; this decomposes at 150—155°. Its composition agrees with the formula of *dihydroxydinitroberberine*, $C_{20}H_{15}(NO_2)_2NO_6$. J. W. L.

Alkaloïds occurring with Cocaïne. By A. EINHORN (*Ber.*, **22**, 399—402).—Liebermann and Giesel (this vol., p. 168) have recently shown that when the amorphous bases occurring with cocaïne are boiled for an hour with hydrochloric acid, they are chiefly converted into ecgonine and acids. This fact has long been known technically. The bases are warmed for three to four days with concentrated hydrochloric acid, the solution is diluted with water, and after separating the acids, concentrated and mixed with ether, whereon most of the ecgonine hydrochloride separates immediately. The filtrate, after freeing from alcohol and ether, is kept for some months so that the rest of the salt may separate, then diluted with water to precipitate small quantities of resinous matter, and again evaporated to a syrup.

The author has investigated a syrup obtained in this manner. It was dissolved in water, separated from resinous substances, mixed with soda and the bright yellow precipitate, which consists chiefly of an amorphous substance, dried and extracted with absolute alcohol. The filtrate from the yellow precipitate contains anhydroecgonine, which can be isolated by acidifying with hydrochloric acid, removing resinous impurities by shaking with ether, evaporating and extracting the crystalline residue with absolute alcohol.

A *chloro*-derivative, probably $C_{26}H_{32}N_3ClO$, is obtained in colourless needles, when the alcoholic extract from the yellow precipitate referred to above is evaporated, the residue boiled with water to remove inorganic compounds, and recrystallised from alcohol with addition of animal charcoal. It melts at 220·5°, and is not changed when warmed with silver nitrate solution. It forms salts with the halogen acids; the *hydrobromide*, $C_{26}H_{32}N_3ClO,3HBr$, crystallises from methyl alcohol in colourless prisms, and has an intensely bitter taste.

When anhydroecgonine is heated at 270° with hydrochloric acid, methyl chloride, hydrocarbons, ammonia, methylamine, and resinous products are formed together with two basic compounds, both of which are volatile with steam (compare Einhorn, this vol., p. 168). These two bases can be separated by dissolving in hydrochloric acid and treating with sodium nitrite. One yields a nitroso-compound which, on decomposing with hydrochloric acid, is converted into a crystalline *hydrochloride*. The other base is not acted on, and is obtained unchanged when the solution is made alkaline and distilled; it yields a sparingly soluble *aurochloride* melting at 212°. A distillate, smelling strongly of pyridine, is obtained when the bases are evaporated with hydrochloric acid, and the residue distilled with zinc-dust. The distillate contains a hydrocarbon and two new bases which can be separated by means of their aurochlorides. The more readily soluble salt melts at 108°; the other contains 46·96 per cent. of gold, and does not melt when heated at 280°. F. S. K.

Oxidation of Gelatin with Potassium Permanganate. By R. MALY (*Monatsh.*, **10**, 26—38; compare Abstr., 1885, 824).—When permanganate (2 parts) is slowly added to gelatin (1 part) at the ordinary temperature, and the mixture is allowed to remain for 14 days, peroxyprotoïc acid is the chief product, and this, on treatment with baryta, splits up into a complex mixture of acids and bases (Abstr., 1888, 1120). When the oxidation takes place in a hot solution, 1 part of gelatin requires 6 parts of permanganate, benzoic and succinic acids being directly formed.

From its furnishing the same oxidation-products, it would appear that gelatin is closely related to egg-albumin in its chemical composition. G. T. M.

Physiological Chemistry.

Reciprocal Action between Hæmoglobin and Protoplasm. By A. SCHWARTZ (*Chem. Centr.*, 1888, 1623, from *Naturwiss. Rundschau, Braunschweig*, 3, 594).—Pure protoplasm, such as blood-corpuscles of the horse or bullock, or the colourless elements of the spleen or lymph glands, when in contact with pure crystallised hæmoglobin, reacts first with formation of methæmoglobin; later the colouring matter is completely decomposed. Hæmoglobin and methæmoglobin, however, are gradually re-formed in the liquid, until at the end of 11 to 14 days more blood colouring matter is formed than was originally present. The coagulation accompanies the reaction in a corresponding manner. The presence of blood serum prevents the destruction of the hæmoglobin altogether, but in other respects does not influence the reaction. J. W. L.

Poisonous Effect of Expired Air. By BROWN-SÉQUARD and D'ARSONVAL (*Compt. rend.*, **108**, 267—272).—The authors have previously shown that the exhalations from the human lung contain some substance or substances capable of exerting a powerful poisonous action (*Compt. rend.*, 1887 and 1888). In the experiments described in this paper, rabbits were placed in a series of air-tight cages so arranged that air entered at one end of the series, passed through each cage in succession, and escaped at the opposite end. The animal in the eighth cage was thus compelled to breathe an atmosphere charged with the products of respiration of the seven others, whilst the animal in the first cage breathed pure air. Under these conditions young rabbits, except those in the first two cages, die rapidly. Those in cages 6, 7, and 8, in fact, die in two or three days. If a rabbit which is nearly dead is removed from its cage it usually recovers after a somewhat long time. The proportion of carbonic anhydride in the air in the second cage is considerably below 1 per cent., whilst in the last cage it will not exceed 3 per cent. Older and larger rabbits resist the action of the poison for a longer time, and in their case the amount of carbonic anhydride in the last cage may rise to 6 per cent.

The authors find that animals of various kinds can breathe without inconvenience air containing a somewhat high percentage of carbonic anhydride.

Men can breathe for two or three hours, without marked discomfort or any permanent effect, air which contains as much as 20 per cent. of carbonic anhydride.

If in the experiments described the air from the sixth cage is passed through tubes containing beads moistened with sulphuric acid, the pulmonary poison is removed, but the carbonic anhydride is not absorbed. When the air thus treated is passed into cages 7 and 8, the animals in these cages live without inconvenience, whilst that in cage 6 dies after a short time. The dead animals show all the symptoms produced by the pulmonary poison, and hence the authors conclude that the injurious effect of expired air is mainly due to the presence of a pulmonary poison or poisons, and not to the presence of carbonic anhydride. (Compare Richardson, Abstr., 1887, 855.) C. H. B.

Influence of Temperature on the Tension of Dissociation of Oxyhæmoglobin. By L. Brasse (*Compt. rend. Soc. biol.*, 5, 660—662).—The tension of dissociation of oxyhæmoglobin is nearly *nil* at 0°. The compound is thus a stable one, giving off its oxygen with great difficulty in a vacuum. It is known also that in hybernating animals the blood is red in the veins as well as in the arteries. The tension of dissociation increases with the temperature; oxyhæmoglobin is only formed when the tension of oxygen in the atmosphere is greater than that of the tension of dissociation. A mammal dies when the temperature of its blood reaches about 45°; at this temperature, the tension of dissociation is still lower than that of the atmospheric oxygen; the composition of the air in the pulmonary alveoli is, however, different from that of the atmosphere. In birds, on the other hand, where, with the arrangement of air sacs, the aëration of the blood is very complete, they do not die until their blood reaches the temperature of 50°.

This paper gives only general conclusions, and is not supported by numerical evidence; the investigations of Hüfner on the same subject (Abstr., 1888, 1214, and this vol., p. 426), published approximately at the same time, are not alluded to. W. D. H.

Action of Hydroxylamine and Nitrites upon Blood-pressure. By T. L. Brunton and T. J. Bokenham (*Proc. Roy. Soc.*, 45, 352—353).—Two of the most striking effects of nitrites are their power (1) to alter the colour of the blood, and (2) to lower the pressure of blood within the vessels. Both these properties are also exhibited by nitroglycerol, and Hay (*Practitioner*, 30, 429) has shown that this is due to the fact that it is decomposed in the blood with evolution of nitrous acid. Hydroxylamine is a substance in which two affinities of nitrogen are saturated by hydrogen instead of by oxygen as in nitrous acid. To render complete the investigation of nitrites and substances allied to them, it was necessary to examine the effect of hydroxylamine on blood-pressure. Raimondi and Bertoni (*Annali*

Univ. di Med., **259**, 97) have already shown that its effect on the colour of the blood is the same as that of the nitrites. In the present research it was found that the effect of lowering blood-pressure is shown by hydroxylamine also. Hydroxylamine hydrochloride (free from nitrite) was the salt used.

W. D. H.

Conversion of Starch in the Human Stomach. By H. ZECHNISSEN (*Bied. Centr.*, 1887, 189—190).—Ewald and Boas hold that in the stomach potato-starch is converted in part into dextrin and maltose, and in part remains unaltered. Dissolved starch in an empty stomach, or, at any rate, in a stomach neutral or slightly acid from hydrochloric acid, is converted into dextrin and maltose. When eggs and water have been previously consumed, then the soluble starch is changed in a manner at present unknown, but at any rate without formation of sugar. E. W. P.

Formation of Glycogen from Carbohydrates. By E. VOIT (*Zeit. Biol.*, **25**, 543—552).—The two theories held with regard to the formation of glycogen are (1) that it is formed by a process of hydration from the food and (2) the so-called economy theory. The latter involves the further hypothesis that glycogen in the body is formed wholly from proteïds. In certain investigations originally undertaken with another object, it was found that there was distinct evidence of the formation of glycogen from the carbohydrates of the food; the experiment was made on a goose which, after a period of four and a half days' inanition, was fed on the following five days on 766·2 grams of dry rice. The animal was killed, and the glycogen in the liver, muscles, and other tissues estimated by Brücke's method—

	Weight.	Glycogen.	
		Total amount.	Percentage.
Liver	205·5 grams	21·6 grams	10·51
Muscles	1327·5 „	17·52 „	1·32
Other tissues (except skin and fat)	382·5 „	5·05 „	—

Supposing that the glycogen of the body had entirely disappeared during the period of inanition, there was thus at least a formation of 44·17 grams during the subsequent five days; this does not take into account any small quantities that might have been present in the skin and fatty tissues, nor the quantity used up by the organism during the five days before death.

From analyses of the urine and fæces during this time, it was calculated that 8·2 grams of nitrogen were excreted, of which 4·7 came from the proteïd matter contained in the rice administered. For every 1 gram of nitrogen in the proteïd of rice, 1·17 grams of carbon would be available for the formation of glycogen, 4·7 grams of nitrogen would therefore correspond with 5·5 grams of carbon, that would account for 12·6 grams of glycogen. The remaining 31· grams of glycogen must, therefore, have been formed from the carbohydrate of the food. W. D. H.

The Formation of Serum-albumin in the Alimentary Canal. By N. Popoff (*Zeit. Biol.*, **25**, 427—452).—v. Ott (*Archiv f. Physiol.*, 1883, 89) showed that the stomach has the power of producing serum-albumin from peptone. In the present experiments, a tortoise's heart removed from the body was kept beating by means of an artificial circulation; the heart was in connection with a mercurial manometer, which was so arranged that a float upon the surface allowed to write on a slowly moving cylinder gave a graphic record of the cardiac contractions. It was found that peptone produced by gastric juice soon brought such a heart to a standstill; but after this solution of peptone had been in the stomach of a living dog for a quarter of an hour, it was capable of keeping the heart beating. This is considered to be sufficient proof that the stomach had in this time reconverted the peptone into serum-albumin. The same result followed if instead of putting the solution of peptone into the stomach it was allowed to remain in a loop of intestine separated from the rest of the alimentary tract by a Vella's fistula. Peptone produced by the pancreatic ferment was not affected in this way, or, to use the phraseology of the authoress, "was not regenerated into serum-albumin." W. D. H.

Synthetic Action of Living Cells. By J. Brinck (*Zeit. Biol.*, **25**, 453—473).—A research of the same nature as the preceding, in which the frog's heart was used instead of the tortoise's heart. On similar grounds it is believed that various forms of animal cells, including certain bacilli, have the power of converting peptone into serum-albumin. W. D. H.

The Relation of Water and Solid Constituents in the Organs and Tissues in Normal and Starving Animals. By S. M. Lukjanow (*Zeit. physiol. Chem.*, **13**, 339—351).—The relation of water to solids was determined in a large number of the organs and tissues of 20 normal pigeons. These are compared with similar investigations on 20 pigeons from which food and water had been withheld for some time. The results are given in tables; and the following are the chief conclusions deduced from them:—

Organs and tissues of the starving animals showed important changes in the relations of solid to water only when the total body weight is diminished by 34 per cent., and the animal had taken no solid or liquid food for 133 hours. The relation in some organs (heart, kidneys, thorax muscles, alimentary tract, blood, brain, and lungs) undergoes little or no change; in others (thigh muscles and bones) the water is increased; and in a third category (spleen, pancreas, liver) the water is diminished. Sex or initial weight are apparently factors which have no influence. W. D. H.

Muscle Pigments. By L. Levy (*Zeit. physiol. Chem.*, **13**, 309—325).—MacMunn (Abstr., 1887, 983) has described a class of pigments occurring in the tissues which, like the hæmoglobin of the blood, have a respiratory function; he has given the name histohæmatin to the class of pigments and myohæmatin to the important member of the class that occurs in muscle. In some muscles, hæmoglobin, as has been shown by many previous observers, also occurs. As a result of the present research, the theory is advanced that hæmoglobin is the only pigment of muscle, and that myohæmatin is merely a derivative of this, and is in fact identical with hæmochromogen. The measurements of the two absorption-bands in wavelengths of hæmochromogen prepared in two ways and of myohæmatin are thus given:—

	1st Band.		2nd Band.	
	Beginning.	End.	Beginning.	End.
Hæmochromogen (prepared by Hoppe-Seyler's method)	5653·00	5473·75	5269·00	5139·15
Hæmochromogen (Stokes' method)	5688·95	5521·55	5354·25	5175·00
Myohæmatin (from dog)	5569·35	5473·75	5210·85	5139·15
Myohæmatin (from pigeon)	5569·35	5473·75	5288·65	5091·35

The myohæmatin bands are thus considerably nearer to the violet end of the spectrum than the hæmochromogen bands; in spite of this, however, the difference is not considered to be sufficiently great to indicate that myohæmatin and hæmochromogen are distinct substances. W. D. H.

Note by Abstractor.—In the course of my own work, I have had occasion to repeat the greater number of MacMunn's experiments; and I can fully confirm his statement that the myohæmatin spectrum, though bearing a superficial resemblance to that of hæmochromogen, is really very different. The difference in the positions of the absorption-bands is, in fact, so marked that the two spectra are easily distinguishable without having resort to measurements. Myohæmatin can also be identified in the fresh muscle by placing it in a compressorium and examining it with the microspectroscope; in such a case there can be no decomposition of hæmoglobin.

W. D. H.

Attraction of Animal Tissues for Sulphur. By J. de Rey-Pailhade (*Compt. rend.*, **108**, 356—357).—The finely divided tissue was digested at 45° with its own weight of sulphur suspended in alcohol, and the hydrogen sulphide evolved was estimated. The quantities of this gas obtained from 100 grams of different tissues were as follows:—

	Muscle.	Kidney.	Spleen.	Bone and marrow.	Adipose tissue.
Rabbit....	1·22	0·94	0·62	0·03	0·01
Dog......	1·39	1·15	1·68	0·02	0·01

These numbers follow the order of the attraction of the various tissues for oxygen. Since the living matter, philothion (Abstr., 1888, 1101), combines with sulphur with formation of hydrogen sulphide, it follows that it should combine with oxygen with formation of water, and it is probable that combination with oxygen is the true function of the philothion, combination with sulphur being merely an incidental phenomenon. C. H. B.

The Salts of Milk and their Relation to the Behaviour of Caseïn. By F. SÖLDNER (*Landw. Versuchs-Stat.*, 35, 351—436).—Two series of determinations of the ash constituents of milk gave the following results in grams per litre of milk:—

	Cl.	P_2O_5.	K_2O.	Na_2O.	CaO.	MgO.
I...	0·820	2·437	1·885	0·465	1·720	0·205
II...	0·980	2·400	1·720	0·510	1·980	0·200

The sulphuric acid was not determined, as it does not pre-exist in the milk, but is produced from the sulphur of the albuminoids; the small amount of iron was also neglected. In grouping the ash constituents as salts, account has to be taken of the fact that a portion of the phosphoric acid found in the ash is derived from the phosphorus of the caseïn; the amount of phosphoric acid to be deducted is 0·581 gram per litre of milk, assuming the latter to contain 3 per cent. of caseïn.

Hammarsten showed that caseïn has acid properties, yielding salts with bases, and obtained a calcium-derivative which contained 0·8 to 1·2 per cent. of lime. The author finds that there are two distinct compounds with calcium; the one, containing 2·39 per cent. of lime, shows an alkaline reaction with litmus, but not with phenolphthaleïn; whilst the other compound does not react either with litmus or with phenolphthaleïn, and contains only 1·55 per cent. of lime. The basicity of caseïn was also determined by titration with soda, using phenolphthaleïn as indicator. Neutral or slightly alkaline solutions of calcium-caseïn, prepared by rubbing together the corresponding amounts of caseïn and calcium carbonate, become turbid only when kept for some time; but when an alkaline calcium-caseïn solution is neutralised or acidified it at once becomes turbid. Alkaline, neutral, or just perceptibly acid solutions of calcium-caseïn do not curdle when boiled; the addition of more acid causes the solutions to curdle, the temperature required becoming lower as the amount of acid present increases. The calcium-derivative which reacts alkaline with litmus is not curdled by rennet. Hence it is probable that caseïn is present in milk as neutral calcium salt (with 1·55 per cent. of lime). Assuming this to be the case, and making the correction for phosphoric acid already given, a litre of milk will contain, in grams—

	NaCl.	KCl.	K_3PO_4.	K_2O.	$Ca_3P_2O_8$.	$Mg_3P_2O_8$.	CaO (in caseïn).
I..	0·877	0·603	1·653	0·405	2·315	0·447	0·465
II..	0·962	0·830	0·903	0·595	2·793	0·436	0·465

The excess of base is probably present in the milk as organic salts, Henkel (this vol., p. 178) having shown that citric acid is a constant constituent of milk to the extent of at least 1 gram per litre. There is reason to suppose that milk contains a still greater amount of organic acid, and this is assumed, for the present purpose, to be citric acid.

Analyses of milk serum, prepared by Zahn's method, by filtering milk through porous battery cells, showed that the whole of the potash, most, if not all, of the soda, and the greater part of the magnesia present in milk are in the form of soluble salts, so that the caseïn salt can only be a calcium-derivative. The acidity of milk to phenolphthaleïn is probably due to the presence of acid phosphates, and to the power of caseïn of uniting with a further amount of base without becoming alkaline towards phenolphthaleïn. Calculated from the results of Series II, the salts present in milk may be grouped as follows (in grams per litre) :—

Sodium chloride.........	0·962	Magnesium citrate......	0·367
Potassium chloride.......	0·830	Dicalcium phosphate....	0·671
Monopotassium phosphate	1·156	Tricalcium ,, ...	0·806
Dipotassium ,, ...	0·853	Calcium citrate.........	2·133
Potassium citrate........	0·495	Lime (in caseïn)	0·465
Dimagnesium phosphate..	0·336		

Hammarsten (*Jahresber. f. Tierchem.*, 1874, 135) considers that caseïn acts as a solvent for calcium phosphate, whilst Eugling (Abstr., 1885, 1083) believes that the caseïn enters into combination with tricalcium phosphate, a view which is also held by Schaffer (*Landw. Jahrb. d. Schweiz*, 1887). Eugling's theory is rejected as being based on erroneous suppositions.

Determinations of lime and phosphoric acid were made in milk, in the serum of milk filtered through porous cells, and in the insoluble portion of milk. 36 to 56 per cent. of the phosphoric acid, and 53 to 72 per cent. of the lime are undissolved, being probably in suspension. The undissolved lime (not in caseïn) is in combination with phosphoric acid as a mixture of di- and tri-calcium phosphates (compare Duclaux, *Ann. inst. nat. agronom.*, 8). It was found that of the undissolved phosphoric acid and lime, 44 to 72 per cent. and 26 to 67 per cent. respectively, could be dissolved in carbonic or acetic acids.

Eugling (*loc. cit.*) states that the calcium salts in milk are not precipitated by ammonium oxalate. The author finds that 85 per cent. of the calcium is precipitated; at the same time there is a change in the appearance of the milk which indicates that the reactions which take place extend to the caseïn, probably with formation of an ammonium salt. Serum obtained by sodium chloride, and that obtained by alcohol, are both precipitated by ammonium oxalate, just like the serum produced by rennet. Eugling's negative result with alcohol serum was, no doubt, due to the presence of alcohol, which is shown to prevent the formation of calcium oxalate.

With regard to the decrease in the acidity in milk, observed by Schaffer (*loc. cit.*) to be produced by the action of rennet, it is found that if the caseïn is made to separate in a finely divided state, so that the whole of it may come into contact with the alkali, and if, at the same time, unnecessary dilution of the curdled milk is avoided, the acidity of the milk remains constant. Boiling has no effect on the acidity of milk.

The belief that caseïn in milk is in combination with calcium phosphate originated in Hammarsten's observation that the curdling of milk by rennet is connected with the presence of calcium salts. Hammarsten showed that other alkaline earths may be substituted for lime, and that they may be present as sulphates and carbonates, and still have the same action (compare Lundberg, *Jahresb. Tierchem.*, 1876, 11). It is shown that calcium phosphate suspended in a caseïn solution does not help the curdling by rennet, but that the presence of a soluble calcium salt is necessary; it is immaterial whether the salt is phosphate or chloride, &c.

According to Mayer (*Milchzeitung*, **10**, 36), when milk is heated at 75° it undergoes a change, and at a still higher temperature, but still much below 100°, it loses its power of being curdled. Experiments made by the author show that milk does not necessarily quite lose the power of being curdled by being heated at 100°, although the time required to curdle milk so treated is much lengthened, especially with milk of less than the usual acidity. The reason that boiled milk will either not curdle at all, or requires a longer time to curdle than fresh milk, is that a part of the dissolved calcium salt is precipitated as tricalcium phosphate. For the same reason curdling of milk by rennet is also prevented, or retarded, by adding more or less alkali. In either case, the property of being curdled by rennet may be restored to the milk by adding acid, passing carbonic anhydride through it, or by the addition of a soluble calcium salt. The author confirms Schaffer's statement that boiled milk treated with carbonic anhydride curdles more quickly than fresh milk.

N. H. M.

Oxyhæmoglobin in the Bile, and the Spectroscopic Characters of Bile. By E. WERTHEIMER and E. MEYER (*Compt. rend.*, **108**, 357—359).—The authors have previously shown that when animals are killed by aniline, toluidine, and other substances which destroy the hæmatics, oxyhæmoglobin appears in the bile. They now find that the same result follows if animals are killed by cold or are subjected to low temperatures. In some of these cases the spectroscopic characters of the bile would seem at first sight to indicate the presence of methæmoglobin, but when reducing agents are added, although the bands of reduced hæmoglobin become visible, the band of methæmoglobin and two bands corresponding with those of oxyhæmoglobin still remain. It follows that the bile under these conditions contains a new modification of methæmoglobin for which the author proposes the name *cholomethæmoglobin.* It seems to be intermediate between the colouring matter of the blood and that of the bile. Cholomethæmoglobin is a normal constituent of the bile of young dogs. Contrary to the usual statement, the bile of dogs of all ages gives the absorption spectrum characteristic of bilicyanin.

C. H. B.

Biliary Acids in Urine during Jaundice. By A. BAELDE and H. LAVRAND (*Compt. rend. Soc. biol.*, 5, 629—630).—In seven cases of jaundice produced in different ways, the biliary acids were always found to be present by means of Pettenkofer's reaction. In two mild cases, the bile pigment disappeared from the urine before the bile acids.

From this, the authors conclude that bile acids occur in the urine in *all* cases of jaundice. W. D. H.

Note by Abstractor.—This conclusion is contrary to that of nearly all previous writers on the subject (Hoppe-Seyler, Gorup-Besanez, Gautier, &c.), and is abundantly contradicted by every-day clinical experience. The authors of the paper just abstracted give no details of the method they adopted. W. D. H.

Urobilinuria and Icterus. By ENGEL and KIENER (*Compt. rend., Soc. biol.*, 5, 678—681).—In contradiction to Hayem (*Soc. méd. des hôp.*, July 22, 1887), the authors find no urobilin in the bile of man, ox, and dog. The bilirubin fixed in the tissues in jaundice is probably there transformed into urobilin, in which form it is more easily eliminated in the urine. This transformation is, however, not constant; the quantity of urobilin which passes into the urine is not proportional to the intensity of the jaundice; and in certain cases, in two of which details are given, a slight jaundice may be accompanied with marked urobilinuria; and an intense jaundice with slight urobilinuria. W. D. H.

The Urine in Melanuria. By R. v. JAKSCH (*Zeit. physiol. Chem.*, 13, 385—394).—The examination of the urine in two cases of melanuria is described. The cases were patients suffering from melanotic sarcoma; and in each case the urine contained a dark brown pigment. The following are the chief conclusions drawn :—The most delicate reagent for detecting melanuria is a very dilute solution of ferric chloride; this colours the urine black. In urine containing melanuria, or its chromogen (melanogen), prussian blue is formed when the urine is mixed with a nitroprusside and aqueous potash, and an acid added. The prussian blue reaction does not seem to depend on the presence of melanin or its precursor; these substances do not give the reaction when they are separated from the urine; it must, therefore, be due to some other substance excreted at the same time, and apparently some substance which is present in minute quantities even in normal urine. The same substance is also abundant in urines which are rich in the indigo-yielding material. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Composition of Bacillus Tuberculosis. By A. HAMMERSCHLAG (*Monatsh.*, **10**, 9—18).—The author finds that the bacillus can be readily cultivated on the surface of a mixture of gelatin and glycerol, in beef-broth containing glycerol, mannitol, grape-sugar, or glycogen, or in a solution of 2 parts of peptone, 6 parts of glycerol, and 1 part of mineral salts in 100 parts of distilled water. If it is considered that the whole of the nitrogen present, after treatment with alcohol, is in the form of albumin (containing 16 per cent. of nitrogen), the composition of the dried bacillus may be taken as 27 per cent. of matter soluble in alcohol, 8 per cent. of ash, 36·9 per cent. of albumin, and 28·1 per cent. of cellulose. Bacillus tuberculosis differs considerably from other bacilli in containing both a large amount of substance soluble in alcohol and ether, and a powerful poison, which may be extracted by exhausting the dried bacillus with alcohol. G. T. M.

Loss of Nitrogen in the Decomposition of Organic Matter. By T. SCHLOESING (*Compt. rend.*, **108**, 205—211 and 261—267).—The substance under investigation was placed in a glass globe with a capacity of 750 to 1000 c.c., and if necessary was mixed with moistened pumice or was moistened with water. To one side of the globe was fused a horizontal glass cylinder, closed at the opposite end, and containing moistened sodium carbonate. A tube bent at a right angle was fused into the opposite side of the globe, its vertical and longer limb dipping below the surface of mercury in a trough. On the upper part of this limb was a bulb which contained a solid acid, such as oxalic acid, to absorb any ammonia that might be evolved. After the introduction of the substance, the globe was made vacuous, and pure air of known composition was admitted. Oxygen was rapidly absorbed, and in order to maintain a sufficient quantity of this gas in the atmosphere of the globe, known volumes of pure oxygen were added from time to time from a special measuring and transferring apparatus. At the end of the experiment, the gas in the globe was extracted, passed into a measuring apparatus after removal of any ammonia or carbonic anhydride that might have escaped absorption, and analysed.

In all the experiments, the atmosphere in the globe remained more or less alkaline in consequence of the evolution of ammonia. The average duration of each experiment was about 13 months.

When lean beef was enclosed in the globe under such conditions that the evolved ammonia remained in the atmosphere, or was dissolved in the liquid which moistened the beef, very little oxygen was absorbed, and very little nitrogen was evolved. If, however, the ammonia was continually absorbed, whilst the atmosphere was kept charged with oxygen, the beef was totally decomposed.

With 13·076 grams of haricot beans 5111·8 c.c. of oxygen was absorbed, and the beans were completely decomposed with the exception of the transparent skins. A considerable quantity of the nitrogen was given off as ammonia, but only 3·0 c.c. of the free gas was evolved. 6·712 grams of cheese absorbed 1687·9 c.c. of oxygen, and gave off 3·9 c.c. of nitrogen, 70 per cent. of the total nitrogen being evolved as ammonia. 8·994 grams of fish absorbed only 936·7 c.c. of oxygen, 84 per cent. of nitrogen being evolved as ammonia, and 2·5 c.c. in the free state. 8·724 grams of horse-dung, containing 1·25 per cent. of nitrogen, was moistened with 20 c.c. of human urine and 20 c.c. of water. This mixture absorbed 183·5 c.c. of oxygen, and liberated 1·8 c.c. of nitrogen, the greater part of the nitrogen being converted into ammonia. In the absence of oxygen, the dung seems to alter but slightly. 100 c.c. of a cultivation of *Aspergillus niger* in Raulin's fluid containing 0·0554 grams of ammoniacal nitrogen and 0·0465 gram of nitric nitrogen, absorbed 2797·4 c.c. of oxygen, and liberated only 0·6 c.c. of nitrogen. 0·0055 gram of ammoniacal nitrogen and 0·0416 gram of nitric nitrogen disappeared. The mould entirely covered the surface of the liquid with its mycelium.

In all cases, the quantity of free nitrogen evolved was small, and hence the results differ from those obtained by J. Reiset. The latter, however, only investigated the earlier stages of the change, whilst in the author's experiments decomposition was always complete, and it is quite possible that the evolution of free nitrogen takes place most freely in the early stages of decomposition. C. H. B.

Slow Combustion of Organic Substances. By T. SCHLOESING (*Compt. rend.*, **108**, 527—530).—The experiments with tobacco (Abstr., 1888, 979) have been extended to temperatures of 80° and 100°. The microbic fermentation, which is very active at 40°, disappears at 75°, and beyond this point the change is entirely chemical, there being no appreciable difference between sterilised and non-sterilised material. The alteration in composition is more rapid the higher the temperature. At 70°, half the nicotine was lost after 52 days, whilst at 80°, 75 per cent. was lost in the same time. At 100°, 75 per cent. of the nicotine was lost in 20 days. The changes essential to the manufacture of snuff become complete in 12 hours at 100°; in 8 to 10 weeks at 70°, and only after several months at 40°. Above 70°, this change takes place with the same rapidity in sterilised and non-sterilised tobacco. During the "fermentation in mass" which is adopted in practice, the useful chemical changes take place without the direct intervention of living organisms. The microbes, by producing fermentation, raise the temperature of the mass to a point at which the activity of the chemical changes becomes sufficiently great to develop the heat necessary for their continuance.

With farmyard manure, the action of microbes is strongly marked even at 75·5°, the amount of carbonic anhydride produced under their influence being 15 times as great as that produced by the purely chemical changes. At 81°, however, the difference between the sterilised and non-sterilised manure becomes inappreciable, and the activity of the microbes ceases. No combustible gases are evolved.

When the manure is heated in a slow current of nitrogen at 52°, the sterilised manure undergoes little change, but that which contains microbes gives off carbonic anhydride, methane, and no hydrogen. At 66°, the evolved gas contains carbonic anhydride and hydrogen, but no methane. The amount of carbonic anhydride is much less than when air is present. C. H. B.

Rôle of Formaldehyde in the Assimilation of Plants. By O. Loew (*Ber.*, **22**, 482—484).—After briefly stating the grounds against Liebig's view that oxalic acid is the first product formed in plants from carbonic anhydride, the author tries to show that Baeyer's theory on this subject is the more probable. The fact, proved by Bokorny, that methyl alcohol can be converted into starch in the chlorophyll cells of algæ is evidence in favour of Baeyer's theory, and the objections raised to this theory, based on the poisonous nature of formaldehyde, may be met by the statement that many plants and bacteria assimilate or produce substances which in slightly larger quantities have a powerfully poisonous action on the organisms themselves. Formaldehyde is so readily condensed that, under certain conditions, it could not accumulate in plants, and for this reason will probably never be isolated from the leaves by distilling. It probably combines with the hydroxy-groups of the active albumin in the protoplasm of the chlorophyll granules immediately after it is formed, and is in some way prevented from reacting with the amido-groups. Graphic formulæ are given showing how the formation of sugar may be supposed to take place. F. S. K.

Sources of the Nitrogen of the Gramineæ and Leguminosæ. By H. Hellriegel and H. Wilfarth (*Ann. Agronom.*, **15**, 5—35, from *Beilageheft Zeitsch. Rübenzucker-Ind.*, Nov., 1888).—This paper contains a fuller account of the experiments referred to in a preliminary note last year (Abstr., 1888, 742). The cultures made in 1883—1887 include barley, oats, peas, buckwheat, lupins, and sanfoin. The pots employed were of glass, with holes at the bottom, and the soil consisted of quartz sand, used for glass making, from 4—8 kilos. being in each pot, and each kilo. containing 0·0027 to 0·0054 gram of nitrogen. The nutrient solution contained definite quantities of potassium phosphate, potassium chloride, magnesium sulphate, and calcium nitrate, containing nitrogen in quantities of 0·000, 0·007, 0·028, 0·056, 0·112, 0·168, 0·224, and 0·336 gram. From 0·1 to 1 per cent. of calcium carbonate was added to the sand, and the plants were watered with distilled water free from ammonia in regulated quantities, so as to keep the percentage of moisture in the soil always within certain limits favourable to growth. The seeds were selected with great care as to uniformity, and were first allowed to germinate, then sown in the pots, and after the seedlings appeared, half were removed from each pot, leaving only those absolutely uniform in size, height, &c. Oats and barley behave alike: without nitrate, there is no development beyond the reserve in the seed, and with varying quantities of nitrate the harvest of dry matter obtained is directly proportional to the nitrate added, and, moreover, the same quantity of nitrate gives always the same weight of dry matter, even in different years. For every milligram of added nitrogen, increases of 93 and 96 milligrams of dry matter are obtained with barley and oats respectively. The harvest always contains less nitrogen than the soil, seed, and manure, taken together, and when the added nitrate is diminished, the nitrogen in the harvest is diminished in the same proportion.

When nitrogen is withheld or is insufficient, the plants do not die, but there is no production of new matter, the new organs, even to the empty grain spikes, being produced solely at the expense of the older leaves, which are successively exhausted and withered.

Sterilisation of the soil and the pots on the one hand, and the addition of the microbes contained in the washings of cultivated soil on the other hand, cause no variation in the above results.

Peas behave quite differently. Some plants languish in a soil deprived of nitrogen, and never develop beyond the reserve material of the seed; but others suddenly acquire new life, develop rapidly, and yield a crop equal in weight to that obtained with a good supply of nitrate, the amount of nitrogen in the crop compared with that contained in the soil, seed, and nitrate (if any), varying from a slight loss to a very large gain (over 1 gram in many instances). This gain occurs also when the pots are placed in a glass cage (as in Boussingault's experiments), the air of which is carefully deprived of all traces of combined nitrogen; it must, therefore, be due to the free nitrogen of the air. When the soil is sterilised by heat, and the pots and seeds by washing with very dilute mercuric chloride, peas behave like oats and barley; there is no gain of nitrogen from the air, but good crops result proportionally to the quantity of nitrate supplied, and no tubercles are formed on the roots. In all cases where there is a gain of nitrogen, tubercles are formed on the roots. Their formation can be rendered certain by adding to the sterilised soil (with or without nitrate) the washings of a small quantity of arable soil, but the kind of soil, or the crop that has been grown in it, greatly affects the result. When these washings are boiled (or even heated to 70°) before being added to the sterilised sand, they are inactive. Thus (the authors infer) the assimilation of free nitrogen from the air by peas, lupins, &c., is not a function of the plant as such, nor can it take place when the growth is in a sterilised medium, but it is connected with the presence of microbes, and with the development of tubercles on the roots. J. M. H. M.

Variations of the Internal Atmosphere of Plants. By J. Peyrou (*Compt. rend. Soc. biol.*, **5**, 699—702).—The composition of the internal atmosphere of plants is always different from that of the air. Oxygen is always present in smaller quantities and carbonic anhydride in larger quantities than in air (*Compt. rend.*, 2nd June, 1885). The gases, however, vary in different plants of the same species, and in different parts of the same plant; from a large number of experiments, the following conclusions are formulated with regard to some of these variations:—

1. The proportion of oxygen in the leaves presents, in the 24 hours, oscillatory movements, in which there are two minima, one between

7 and 9 A.M., and the other between 4 and 6 P.M.; and two maxima, one about midday, the other about midnight. These movements are independent of the seasons, of the action of chlorophyll, and of the atmospheric temperature. The maximum of the night is generally higher than that of midday.

(2.) The proportion of oxygen increases in the leaves on agitating them with the air.

(3.) The proportion of oxygen varies with age; the young leaves enclosing less than the adult leaves, and these less than the etiolate leaves.

(4.) The proportion of oxygen is less in plants grown in the sunlight than in those grown in the dark.

(5.) Plants with persistent leaves inclose more oxygen than deciduous or annual plants.

(6.) The coloration of the leaves has no influence on their gaseous contents.

(7.) The absolute quantity of carbonic anhydride is greater than the diminution in the quantity of oxygen in proportion to nitrogen.

(8.) Any condition unfavourable to the development of the plant increases the proportion of oxygen; the opposite condition diminishes it.

(9.) The quantity of carbonic anhydride given out is less than that of the oxygen absorbed; there is thus a real assimilation of the oxygen. W. D. H.

Products of the Decomposition of Albuminoïds in Plants. By W. PALLADIN (*Chem. Centr.*, 1889, 23, from *Ber. deut. botan. Gesell.*, **6**, 296—304).—Experiments carried out to determine the nature of the products of the decomposition of albuminoïds in wheat in the absence of free oxygen, showed these to be principally tyrosine and leucine with very little asparagine. The last-named substance is present in the plant during the first few days, but becomes changed to ammonium succinate when the plant dies. Considerable quantities of asparagine can only be formed from the albuminoïds in the presence of free oxygen; it is thus the result of oxidation, and not of dissociation. J. W. L.

Decomposition of Proteïds in Green Plants kept in the Dark. By E. SCHULZE and E. KISSER (*Landw. Versuchs-Stat.*, **36**, 1—8).—The formation of asparagine in green portions of plants kept in the dark was observed by Borodin and confirmed by Müller (*ibid.*, **33**, 311), whilst the simultaneous loss of proteïds was proved by experiments made by Schulze and Bosshard (*ibid.*, **33**, 117). The object of the experiments described in the present paper was to determine whether this decomposition of proteïds also takes place in growing plants when light is excluded. Oat plants, in pots, were allowed to grow until 45 or 50 cm. high; half of the plants were then cut down just above the ground and quickly dried. The remaining plants were kept in a dark room for seven days, and then cut and dried like the others. The plants which had been kept in the dark were partially yellow, but some of the leaves had a fairly bright green colour. The following analytical results were obtained with the plants not kept in the dark (*a*) and with those kept in the dark for seven days (*b*). The numbers represent the percentages in dry substance:—

	a.	*b*.
Total nitrogen	3·43	3·60
Nitrogen as proteïds	2·64	1·44
Non-proteïd nitrogen	0·79	2·16

The decomposition of proteïds was, therefore, very considerable. The oat plants which had been kept in the dark were examined for asparagine, which was separated and determined by Sachsse's method. The amount of nitrogen present in asparagine (and glutamine?) was 0·713 per cent., corresponding to 59 per cent. of the nitrogen of the decomposed proteïds. Besides asparagine (and glutamine?), compounds of the xanthine and hypoxanthine groups seem to be formed.

The plants which were not kept in the dark contained only traces of amides.

Attention is drawn to a paper by Palladin (*Ber. deut. botan. Gesell.*, **6**, 205), containing the results of experiments which further confirm the results of Borodin and Schulze, and also to experiments on the decomposition of albuminoïds in plants in an atmosphere free from oxygen (preceding Abstract). N. H. M.

Occurrence of an Insoluble Carbohydrate in Red Clover and Lucerne. By E. SCHULZE and E. STEIGER (*Landw. Versuchs-Stat.*, **36**, 9—13).—It was previously shown (Abstr., 1887, 460) that the seeds of *Lupinus luteus* contain an insoluble carbohydrate (paragalactin), which, when heated with dilute acids, yields galactose, and is converted by the action of nitric acid into mucic acid. A carbohydrate having similar properties is found to be also present in red clover and lucerne.

The finely powdered, air-dried, red clover (200 grams), which was cut when in full flower, was extracted with a mixture of ether and alcohol and treated with a malt extract at 50—60°. The solution was removed by means of a pipette, and the residue treated with cold 0·4 to 0·5 per cent. aqueous potash; after removing the potash, the residue was washed with water until no longer alkaline. The substance was boiled with 2½ per cent. sulphuric acid and the sugar determined. The amount of sugar, calculated as dextrose, was found to be 6·06 grams. When the sugar is evaporated down to a syrup, dissolved in nitric acid (sp. gr. = 1·15) and evaporated on a water-bath, a considerable quantity of mucic acid is obtained; it is therefore probable that the sugar solution contains galactose, as this is the only known glucose which is converted by nitric acid into mucic acid. As more than one sugar is present, an exact determination was not possible, and the number given above can only be considered as approximate.

Air-dried lucerne (100 grams), treated in the manner described above, yielded 2·476 grams of sugar, calculated as dextrose. The sugar, when oxidised with nitric acid, yielded mucic acid, but much less than the sugar from red clover. N. H. M.

Soluble Carbohydrates in the Seeds of Leguminous Plants. By W. MAXWELL (*Landw. Versuchs-Stat.*, **36**, 15—21).—Very finely powdered seeds of *Faba vulgaris* (600 grams) were extracted three times with hot 70 per cent. alcohol, and the soluble carbohydrates separated by Schulze's method. Cane-sugar and a substance having the properties of a galactose were found.

The seeds of *Vicia sativa* also contain cane-sugar and a galactose.

The seeds of *Pisum sativum* yielded an extract which gave the same reactions as those for the seeds of *Faba vulgaris* and *Vicia sativa*, and may, therefore, be presumed to contain the same compounds.

The total amount of soluble carbohydrates was determined by extracting the finely powdered seeds with water at 37—40°, filtering and precipitating the filtrate with a small amount of phosphotungstic acid, and again filtering. The solution was boiled with hydrochloric acid for three hours (compare Sachsse, *Chem. Centr.*, 1877, 732) and the sugar determined by titration with Fehling's solution. Owing to the presence of sugars of unequal reducing power, the results are only approximate; the sugar found in the extract was calculated as dextrose, and then the number reduced to a carbohydrate of the formula $C_6H_{10}O_5$. The following are the mean percentages of soluble carbohydrates in dry substance:—*Faba vulgaris*, 4·227; *Vicia sativa*, 4·851; *Pisum sativum*, 6·218 (compare Stingl and Morawski, Abstr., 1886, 829, and 1887, 686; O'Sullivan, Trans., 1886, 58 and 70).

N. H. M.

Morphine in Escholtzia Californica. By BAUDET and ADRIAN (*Chem. Centr.*, 1889, 197, from *Pharm. Zeit.*, **34**, 23).—This plant, which belongs to the Papaveraceæ, has been used in America as a substitute for opium. The authors have found morphine in it, in addition to another base and a third substance, probably a glucoside.

J. W. L.

New Source of Coumarin. By H. MOLISCH and S. ZEISEL (*Chem. Centr.*, 1889, 17, from *Ber. deut. botan. Gesell.*, **6**, 353—358). —Coumarin has been found in the plant, *Ageratum mexicanum*, one of the Compositæ. During life the plant does not smell of coumarin, but the odour is apparent after death. In what state of combination it occurs, the authors could not determine. The principal part is found in the leaves; the blossoms and roots containing but very little.

J. W. L.

Andromedotoxin in the Ericaceæ. By P. C. PLUGGE (*Arch. Pharm.* [3], **27**, 164—172).—Generally the parts of the plants were cut up and extracted with water, the infusion was purified by means of neutral and basic lead acetate, the lead removed by hydrogen sulphide, and the solution, after concentration in a vacuum, repeatedly shaken up with chloroform. Both chemical and physiological tests for the detection of andromedotoxin were applied to the residue obtained on evaporating the chloroform solution. So far, the following plants have been found to contain andromedotoxin:—*Andromeda japonica*, *A. polifolia*, *A. catesbaei*, *A. calyculata*, *A. polifolia augustifolia*, *Rhododendron ponticum*, *R. chrysanthemum*, *R. hybridum*, *R. maximum*, *Azalea indica*, and *Kalmia latifolia.* The following do not contain andromedotoxin:—*Rhododendron hirsutum*, *Ledum palustre*, *Clethra arborea*, *C. alnifolia*, *Arctostaphyllos officinalis*, *Chimaphila umbellata*, *Oxydendron arboreum*, and *Gaultheria procumbens*. J. T.

Lecithin in the Seeds of Plants. By E. SCHULZE and E. STEIGER (*Zeit. physiol. Chem.*, **13**, 365—384).—The estimation of the amount of lecithin from the percentage of phosphorus in the ethereal extract of powdered seeds has given very variable results, both in the hands of previous investigators and in the commencement of the present research. The reason for this appears to be that the treatment of the finely powdered seeds with cold ether only dissolves part of the lecithin present; hot alcohol dissolves a considerable quantity of a substance rich in phosphorus from the seeds after their treatment with ether; on evaporating to dryness the alcoholic extract thus obtained, a residue is left which is largely soluble in cold ether, and from which fatty acids and choline aurochloride were prepared. It is, therefore, lecithin. This lecithin probably exists in the condition of a loose combination with some other substance in the seeds, and this compound is decomposed by treatment with boiling alcohol. Bearing this source of error in mind, a number of quantitative estimations were made:—

	Contained in dry seed substance.	
Seeds of	Phosphorus in ether-alcoholic extract, per cent.	Lecithin, per cent.
Lupinus luteus	0·060—0·061	1·55—1·59
Soja hispida	0·063	1·64
Vicia sativa	0·047	1·22
Faba vulgaris	0·031	0·81
Triticum vulgare	0·025	0·65
Secale cereale	0·022	0·57
Hordeum distichon	0·028	0·74
Linum usitatissimum	0·034	0·88

In further researches, it was shown that etiolated lupin buds contain much less lecithin than the seeds; that is, a considerable amount of this substance is used up during the process of germination and growth. W. D. H.

Influence of Carbonic Oxide on Germination. By G. LINOSSIER (*Compt. rend. Soc. Biol.* **5**, 565—566).—Seeds of cress, lettuce, and millet were grown in artificial atmospheres consisting of oxygen (which was always present in the proportion in which it exists in the atmosphere), nitrogen, and carbonic oxide in variable quantities. Some specimens were exposed to the light, others grown in the dark. They were also grown in different conditions of temperature. It was found that the plants germinated perfectly well, and in the light, chlorophyll grains appeared in an atmosphere containing as much as 79 per cent. of carbonic oxide. When such a large proportion of

carbonic oxide is present, the germination is a little slower than in the air; but 50 per cent. or less of the gas makes no appreciable difference; germination occurs as quickly as in atmospheric air. Claude Bernard (*Leçons sur les effets des subst. tox. et medic.*, p. 200) found that air containing a sixth of its volume of carbonic oxide stopped germination: it is probable that the gas he used was impure, and that the deleterious effect on vegetation was due to such impurity.
W. D. H.

Fertilising Properties of the Water of the Nile. By A. Müntz (*Compt. rend.*, **108**, 522—524).—The Nile water at the time of rising on September 6th, 1888, contained in solution per cubic metre—

N_2O_5.	P_2O_5.	K_2O.	CaO.
4·10	0·40	3·66	48·00

The same water at a depth of 0·6 metre in the middle of the Great Nile contained during the time of rising from 1·7 to 2·5 kilos of suspended matter per cubic metre, the mean being 2·2 kilos. This consisted mainly of clay, calcium carbonate, and organic matter, and had the following percentage composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	K_2O.	MgO.	$CaCO_3$.	P_2O_5.	Organic matter.	H_2O.
53·07	14·57	10·21	6·37	1·07	3·13	0·19	2·87	7·41

The organic matter contained 0·11 of organic nitrogen, and 0·31 of the potassium oxide was soluble in acids. This analysis differs from those of previous observers, especially in the low proportion of organic matter. Probably the earlier investigators regarded the total loss on ignition as due to organic matter. The mud is very finely divided, and hence its constituents are in a very readily assimilable form. The calcium carbonate present prevents the clay from caking, and thus keeps the mass porous.

It is evident that the suspended matters of the water and not the dissolved constituents are the chief fertilising agents. The following table shows the quantity of useful constituents in solution and in suspension per cubic metre.

	N.	P_2O_5.	K_2O.	CaO.
In solution.........	1·07	0·40	3·66	48·00
In suspension	3·00	4·10	150·00	70·50

C. H. B.

Manuring of Rice. By C. C. Georgeson (*Bied. Centr.*, 1889, 167—169).—There is considerable difficulty in manuring rice grown on irrigated land, but the author has applied ammonium sulphate, potassium carbonate, and superphosphate to several plots, and found the best results to follow from an application of these three compounds, according to the requirements of the plant as indicated by the composition of the soil. Ammonia greatly increased the growth but not the yield of grain, and if this manure were in excess then the size and weight of the grains suffered, and the straw was increased at the expense of the grain; on the other hand, the quantity of grain was increased by the superphosphate whilst potash took up a medium position as to effectiveness.

The manuring of rice grown on volcanic tufa was easier of accomplishment than when the land was under irrigation; nitrogenous manuring when alone or in combination had no effect, but potash and superphosphate are capable of increasing the yield of grain. One point was especially noticed, that the rice grown on the tufa bore a smaller amount of corn in proportion to the straw than did that grown on irrigated land. E. W. P.

Cultivation of Potatoes. By A. GIRARD (*Compt. rend.*, **108**, 525—527).—A large number of experiments show that although small tubers may have great reproductive power, the weight of the yield is comparatively small. Medium-sized tubers, however, give practically the same result as the largest, and are therefore the most suitable for seed. It is important to select the seed tubers from heavy roots, since even large tubers from small roots usually give inferior crops. The power of producing a satisfactory yield seems in fact to be hereditary. It is found that the heaviest roots are associated with the most vigorous aërial vegetation. C. H. B.

Assimilation of the Phosphoric Acid in Basic Slag. By PETERMANN (*Bied. Centr.*, 1889, 158—165).—Basic slag has been compared with superphosphate and with sodium nitrate and potassium chloride, separately and mixed with phosphates; the crops were spring wheat and oats; the land light and heavy. As a result, it was found that when other food constituents were present in sufficient quantity, the phosphate of basic slag was readily assimilated, and the increased yield on land containing only 0·1 per mille P_2O_5 was very great, whilst it was less so on land containing 0·65 per mille; in fact, no recognisable difference was noticed between the two phosphates; the calcium present in the basic slag seems to have no separate action, as it has been supposed to have, even on land poor in lime (1·55 per mille), neither are the iron oxides present in any way detrimental to the formation of sugar or starch in sugar-beet or potatoes. On land poor in phosphates, sodium nitrate or potash produced no effect unless basic slag or superphosphate was also added. E. W. P.

Manuring with Fish Guano. By PETERMANN (*Bied. Centr.*, 1889, 165—167).—Fish guano (free from fat) when mixed with kainite or alone, was found to be a good and paying manure for potatoes; no increase of diseased tubers was noticed. E. W. P.

Analytical Chemistry.

Detection of Free Sulphuric Acid in Aluminium Salts. By E. EGGER (*Zeit. anal. Chem.*, **27**, 725—728).—The colour reactions obtained by warming a mixture of cholic acid and cane-sugar with sulphuric acid have been shown by Mylius to result from the formation of furfuraldehyde, of which substance 1 part in 20,000 of water is sufficient to produce the effect. Furfuraldehyde and sulphuric acid produce red colours with the following substances also :—Isopropyl alcohol, isobutyl alcohol, allyl alcohol, trimethyl carbinol, dimethyl ethyl carbinol, amyl alcohol, oleïc acid, petroleum; but not with ethyl alcohol, normal propyl alcohol, capryl alcohol, acetic acid, isobutyric acid, acraldehyde, or benzene. A mixture of cholic acid and furfuraldehyde is likewise a most delicate reagent for sulphuric acid, a distinct red colour being produced by 1 c.c. of $\frac{N}{1000}$ acid. To detect free acid in a salt, the substance is powdered, moistened with water, and digested with ether-alcohol, which after 24 hours is filtered off and evaporated to 1 c.c. before adding the cholic acid and furfuraldehyde. Using 20 grams of substance, the reaction appears capable of detecting 0·016 per cent. of free acid, but in aluminium sulphate 0·03 per cent. is the limit.

Jorissen's test, as used by Hager (Abstr., 1887, 182), is much less sensitive, requiring about 10 times as much acid, whether alone or mixed with magnesium sulphate. With zinc sulphate, aluminium sulphate, and alum, however, carefully freed from acid, the reaction was always obtained when the salt was reduced to the finest powder, but not when it was only coarsely crushed. M. J. S.

Estimation of Phosphorus and Sulphur in Iron. By M. A. v. REIS (*Chem. Centr.*, 1889, 115, from *Stahl u. Eisen*, 8, 827—831). —After washing the ammonium phosphomolybdate precipitate on the filter with dilute nitric acid, the author recommends that it shall be dissolved in 15 c.c. of ammonium citrate (solution, prepared by dissolving 10 grams citric acid in 100 c.c. ammonia, sp. gr. 0·91) and finally washed with dilute ammonia. Phosphoric acid is then precipitated as ammonium magnesium phosphate, which is free from iron under these circumstances. The sulphur is determined by fusing 5 grams of the iron with 5 grams of a mixture of magnesia and sodium carbonate (2 pts. to 1 pt.) for 10 minutes; after cooling again, the mass is pounded up, and again fused, with frequent stirring. After cooling, the mass is digested with water, the solution oxidised with hydrogen peroxide, and the sulphuric acid precipitated with barium chloride.

J. W. L.

Estimation of Nitrogen by Kjeldahl's Method. By E. AUBIN and ALLA (*Compt. rend.*, **108**, 246—248).—The results obtained by this method were compared with those obtained by means of soda-lime. The soda-lime used was prepared by slaking 600 grams of calcium oxide with a solution of 300 grams of sodium hydroxide in an equal weight of water; 25 to 30 grams of soda-lime were mixed with 0·5 gram of the substance, and a layer of 50 mm. of granular soda-lime was placed before and behind the mixture in the combustion tube. If too small a quantity of soda-lime is used, the results are too low, and this cause has greater influence than differences in the mode of heating. With Kjeldahl's method, 0·5 gram of substance was heated with 20 c.c. of strong sulphuric acid and 0·5 c.c. of mercury.

The substances examined included caseïn, albumin, grains of cereals, legumes, forage plants, urea, alkaloïds, and soils, and in all cases the quantity of nitrogen obtained by Kjeldahl's process was equal to that obtained with soda-lime, and in many cases it was higher.

C. H. B.

Source of Error in the Estimation of Nitrogen by Kjeldahl's Method. By M. Zecchini and A. Vigna (*Chem. Centr.*, 1888, 1628, from *Staz. sperim. agric. ital.*, **15**, 298—304).—In order to prevent a loss of ammonia when neutralising the sulphuric acid mixture with alkali, the authors recommend that the latter shall be introduced into the liquid through a funnel, after the flask has been connected with the condenser. It is also recommended to pass a current of air through the apparatus. J. W. L.

Estimation of Total Nitrogen in Urine. By O. de Coninck (*Compt. rend. Soc. biol.*, 5, 540—541).—It is found in comparative estimations of the total nitrogen in urine by the methods of Kjeldahl and of Dumas, that they do not give concordant results when the urine contains certain alkaloïds. The three alkaloïds specially studied were pyridine, picoline, and lutidine; these three compose a homologous series, and lend themselves very well to comparative experiments, as they have about the same solubilities, and are eliminated in approximately equal quantities in the expired air, in the saliva, and in the urine.

The proportion of total nitrogen in such urine is from 2—3½ per cent. lower by Kjeldahl's method, and this loss increases with the molecular weight of the alkaloïd employed. This appears to be of some importance when it is considered that the simplest ptomaïnes yet isolated contain eight atoms of carbon. In urine containing ptomaïnes (and the same is true for leucomaïnes), Kjeldahl's method, therefore, is likely to produce serious errors. W. D. H.

Estimation of Ammonia (ready formed) in Manures. By M. Zecchini and A. Vigna (*Chem. Centr.*, 1888, 1628—1629, from *Staz. sperim. agric. ital.*, **15**, 276—290).—The authors find that if magnesium ammonium phosphate is distilled with magnesia, all the ammonia is not set free, and therefore when determining the amount of ready formed ammonia in manures, &c., they should be previously treated with cold dilute hydrochloric acid, after which all the ready formed ammonia may be set free by magnesia and distilled off.

J. W. L.

Detection of Nitrates in Soil. By B. Frank (*Bied. Centr.*, 1889, 148—149).—Frank (this vol., p. 71) has stated that sand grains in soil give indications of the presence of nitrate with diphenylamine, whereas Kreusler (this vol., p. 547) denies this, and attributes the reaction to the presence of manganese and iron oxides. In this article, Frank repeats his statements, and declares that on those spots where ferric oxide occurs the diphenylamine remains colourless; he does not allow that the non-appearance of the blueing after the ignition of the sand is any proof of the absence and destruction of the nitrate.

E. W. P.

Detection of Minute Quantities of Arsenic. By F. A. Flückiger (*Arch. Pharm.* [3], **27**, 1—30).—Gutzeit's method is far more sensitive than any other; this is based on the formation of the yellow compound, $AsAg_3,3NO_3Ag$, by the action of arsenious hydride on silver nitrate; under the action of water, the yellow compound becomes black, owing to the formation of arsenious oxide and metallic silver. A convenient apparatus consists of a glass cylinder, 10 cm. high, about 25 c.c. capacity, and with a neck of 1½ cm. diameter. For the production of hydrogen, hydrochloric acid of 1·036 sp. gr. (7·3 per cent. HCl) with small bars of pure zinc, or sulphuric acid of 1·055 sp. gr. (8⅓ per cent. H_2SO_4) may be used; 4 c.c. of the acid and 1 gram of the zinc give a moderate and sufficient current. The mouth of the vessel is covered with a couple of layers of filter-paper twisted about the neck. A small piece of filter-paper is now moistened by means of a single drop of a saturated solution of silver nitrate, which has been slightly acidified with nitric acid, and is twisted over the other two layers. If no yellow stain appears within an hour, the underside of the paper is also examined. It is well to conduct the operation away from too much light. The reaction is exceedingly sensitive; 0·001 milligram of arsenious anhydride can be well detected. Mercuric chloride is almost as sensitive as silver nitrate as indicator for this process, with the advantage that the yellow stain thus produced is not affected by light and water. Sodium-amalgam and other reagents were tried for the generation of hydrogen, but the process described was found most suitable. The presence of a trace of sulphide in the zinc may cause error both with silver nitrate and mercuric chloride. The purity of the zinc should therefore be ascertained by treating 10 grams for two hours in the absence of light, when no change should appear in silver or mercury paper. It is very desirable that zinc bars of 5 mm. diameter at the most should be obtainable, which by the above test would give no indications of sulphur, arsenic, phosphorus, or antimony. The application of the process in various directions is shown; it is much more sensitive than Marsh's test, and gives comparable results in a short time.

J. T.

New Test for Carbonic Oxide Poisoning in Blood. By K. Katayama (*Chem. Centr.*, 1888, 1633, from *Virchow's Archiv*, **114**, 53—64).—The blood is diluted with 50 vols. of water, and to 100 c.c. of this liquid 0·2 c.c. of yellow ammonium sulphide (100 grams of fresh, colourless ammonium hydrosulphide with 2·5 grams sulphur), and 0·2—0·3 c.c. of 30 per cent. acetic acid are added, and the whole gently mixed. Blood containing carbonic oxide causes a bright red coloration, whereas with normal blood the colour is greenish-grey.

The spectroscopical analysis shows that the spectra of sulphomethæmoglobin and carbonic oxide hæmoglobin are combined.

J. W. L.

Volumetric Estimation of Carbonic Acid. By E. Jäger and G. Krüss (*Zeit. anal. Chem.*, **27**, 721—724).—The carbonate, contained in a flask connected with a Hempel's burette, is decomposed by somewhat concentrated hydrochloric acid (sp. gr. 1·001) delivered from a small burette whose jet passes through the cork of the flask. The smallest possible volume of acid is used, so as to reduce the correction for solubility of the gas in the saline solution produced to an amount which may safely be neglected. M. J. S.

Estimation of Carbonic Anhydride in Air. By F. Schydlowski (*Zeit. anal. Chem.*, **27**, 712—721).—The method is based on the fact that gases of unequal specific gravity separated by a porous plate will diffuse until a certain difference in pressure on the two sides of the plate is attained. A glass cylinder filled with soda-lime and crystallised calcium chloride is covered by a glass plate having the porous plate at its centre. Upon the glass plate stands a bell-jar, through which the air, dried by crystallised calcium chloride, is aspirated. A pressure gauge containing petroleum shows the difference of pressure in the two vessels. Since the carbonic anhydride which diffuses through the plate is immediately absorbed by the soda-lime, the difference of pressure is proportional to the percentage of carbonic anhydride in the air in the bell-glass. The value of the scale is ascertained by substituting concentrated sulphuric acid for the soda-lime, and filling the bell-glass with air saturated with water-vapour at a known temperature. The apparatus then serves as a hygrometer. On dividing the reading of the pressure-gauge by the tension of the water-vapour, the quotient is the diffusion value (a) of the porous plate. This is different for every plate, but for the same plate remains constant for years. The percentage of carbonic anhydride (x) in a specimen of air is then given by the formula $x = \frac{100c}{a \times k}$, where c is the difference in pressure in the two vessels as shown by the gauge, and k the barometric pressure (in millimetres of mercury) at the time. Comparison of the indications of the instrument with gravimetric determinations covering a wide range, shows an agreement sufficiently close for practical purposes. M. J. S.

Detection of Mercury. By J. Klein (*Arch. Pharm.*, **27**, 73—77).—The test employed is the converse of Nessler's ammonia test. If a mercuric chloride solution is treated with potassium iodide until the solution again becomes clear, then with sodium hydroxide, and finally with a few drops of ammonium chloride solution, a yellow or brown turbidity arises according to the amount of mercury present. The limit of the test for mercuric chloride is about 1 : 31,000, whilst the stannous chloride test has a limit of about 1 : 40,000 to 50,000. The former test may, however, on account of its characteristic colour, very well supplement the latter. The test can be applied to blood, urine, and other organic substances after oxidising with hydrochloric acid and potassium chlorate. J. T.

Analysis of Mixtures containing Aluminium, Calcium, and Magnesium. By L. BLUM (*Zeit. anal. Chem.*, **27**, 706—712).—In an earlier communication, the author recommended the precipitation of the alumina by the addition of only a small excess of ammonia, which was not to be boiled out completely (Abstr., 1888, 324). He now compares results obtained by this process with those of a double precipitation as prescribed by Fresenius. In the second precipitation, much ammonium chloride was present, owing to the necessity for the use of much hydrochloric acid in dissolving the precipitate. The double precipitation yielded lower numbers for the aluminium, owing to the more complete removal of the calcium and magnesium, but the calcium also came out lower, as did also the sum of the three bases. The magnesium was higher. The total loss is traceable to the solubility of both calcium oxalate and magnesium ammonium phosphate (chiefly the latter) in strong ammonium chloride solutions. In cases of double precipitation, it is therefore necessary to remove the ammonium salts by ignition before precipitating the magnesium. M. J. S.

Separation of Zinc from Nickel. By H. BAUBIGNY (*Compt. rend.*, **108**, 236—238).—The author has previously shown (this vol., p. 346) that the quantity of free sulphuric acid required to prevent the decomposition of zinc sulphate by hydrogen sulphide varies with the volume of the liquid. When the quantity of free acid present does not exceed five or six times the weight of the acid in the salt, the method is available in analysis, and if the solution is sufficiently dilute, practically all the zinc is precipitated after saturating the liquid with hydrogen sulphide and allowing it to remain for about eight hours. Acetic acid does not dissolve zinc sulphide, and even if present to the extent of 25 per cent. it does not prevent the precipitation of the sulphide from the sulphate provided the liquid contains no free sulphuric acid. Previous observations have shown that these facts may be utilised for the separation of zinc from cobalt, nickel, and other metals which are not precipitated by hydrogen sulphide in presence of acetic acid.

The operation is conducted with an acetic acid solution of the sulphate containing not more than 3 grams of salt per litre. After saturating with hydrogen sulphide, it is allowed to remain two to three hours, and the precipitate is washed with 10 per cent. acetic acid containing hydrogen sulphide. The nickel in the filtrate is thrown down in the usual way by heating it to 70—75°, and allowing it to remain in a closed vessel after saturating with hydrogen sulphide. No acid except acetic acid must be present in the free state, and, if necessary, ammonium acetate may be added to the solution.

If the quantity of nickel present does not exceed one-third that of the zinc, the addition of acetic acid is not necessary, since the sulphuric acid liberated from the zinc sulphate keeps the nickel in solution. C. H. B.

Separation of Zinc from Cobalt. By H. Baubigny (*Compt. rend.*, **108**, 450—453).—The method of separation by means of hydrogen sulphide which succeeds in the case of nickel and zinc (preceding Abstract) is not applicable in the case of cobalt and zinc, unless the proportion of cobalt is very small. The zinc sulphide carries down cobalt sulphide even under conditions in which cobalt alone would not be precipitated. This result seems to be due to a secondary action of the zinc sulphide on the cobalt sulphate.

A fairly accurate estimation can, however, be made if the liquid contains a quantity of free sulphuric acid equal to the quantity of combined acid in the cobalt and zinc sulphates. The separation is not quite complete, but if one of the metals is present in small proportion the error is very small. In other cases, the first precipitate of zinc sulphide should be reconverted into sulphate and the process repeated.

C. H. B.

Separation of Nickel from Cobalt. By R. Fischer (*Chem. Centr.*, 1889, 116, from *Berg. Huttenm. Zeit.*, **47**, 453).—A rapid method for the separation of these metals is the following:—The alkaline (potash) solution of the two oxides is boiled with hydrogen peroxide, which oxidises the cobalt to sesquioxide. After cooling, potassium iodide is added, then hydrochloric acid, and the solution is titrated with sodium thiosulphate. J. W. L.

Detection of Manganese. By J. Klein (*Arch. Pharm.* [3], **27**, 77—79).—Small quantities of manganese may be detected by the precipitate or dark coloration which is obtained on the addition of hydrogen peroxide to an alkaline or ammoniacal manganese solution. Cobalt is the only element that reacts similarly. An excess of ammonium chloride and ammonia reduce the sensitiveness of the test; if these be replaced by sodium hydroxide, the sensitiveness increases.

J. T.

Destruction of Organic Matters in Toxicological Investigations. By F. Marino-Zucco (*Chem. Centr.*, 1888, 1598, from *Rend. Acad. dei Lincei* [4], **4**, 203—207).—The substance is covered with concentrated nitric acid, and nitrogen tetroxide is passed into the mixture, heat being applied when the liquid has become green. 1 kilo. of meat may be completely destroyed in half an hour, and the fat may be removed from the surface after cooling. Experiments with definite quantities of arsenic, copper, and zinc showed that the method is well suited for the purpose. J. W. L.

Cyanogen and its Compounds in the Products of Coal Distillation. By M. A. Pendrié (*Chem. Centr.*, 1889, 43, from *J. Gasbeleucht. u. Wasserversorgung*, **31**, 1006—1010).—The author recommends the following method for the determination of the cyanogen compounds formed in the distillation of coal. Ammonia water is acidified with nitric acid, and precipitated with argentic nitrate, the precipitate collected, dissolved in ammonia, and reprecipitated with nitric acid, and the weight of the cyanide and thiocyanate determined; it is then dissolved in potassium cyanide and the sulphur oxidised to sulphuric acid, which is determined as barium sulphate. From these data the amounts of cyanide and thiocyanate are obtained. The hydrogen sulphide is determined by means of N 1/10 zinc chloride; the hydrogen thiocyanate in the filtrate is precipitated with argentic nitrate, and the total sulphur finally determined by oxidation with bromine. J. W. L.

Examination of Spirituous Liquids. By J. TRAUBE (*Zeit. anal. Chem.*, **28**, 26—45).—The author, whilst adopting the principle of Elsworthy's inclined capillarimeter (Trans., 1888, 102), prefers the original form of his own apparatus, giving an oblique position only to the upper part of the tube and scale. The angle of inclination in the instruments made under his instructions is such as to give differences two or three times as great as in the original form. The form of stalagmometer figured in the *Berichte* (**20**, 2646), whilst giving drops of great uniformity, is difficult to construct, on which account many of the instruments sent out agree only approximately with the published tables. A return to the earlier form (*Ber.*, **19**, 1872) with a capillary point is recommended. For concentrating the fusel oil in a small portion of the solution, potash is found more advantageous than ammonium sulphate (Abstr., 1888, 92). As little as 0·02 or 0·03 per cent. of fusel oil can be detected in a 20 per cent. spirit by the stalagmometric method without concentration, but by using a potash solution of appropriate strength (sp. gr. 1·24), less than 1 part of fusel oil in 10,000 can be quantitatively estimated.

Röse's method of determining fusel oil consists in shaking the spirit with chloroform, the volume of which increases proportionally to the fusel oil present. Other impurities, such as aldehyde, also augment the volume of the chloroform, and that to a greater extent than fusel oil, whilst their influence on the capillarimetric and stalagmometric methods is extremely small.

The vaporimetric method is highly suitable for estimating the more volatile impurities. The first runnings consist in great part (80 per cent.) of aldehyde. The presence of this substance increases the vapour-tension of alcohol of every strength. The effect of fusel oil on the vapour-tension depends on the proportion of water present. With less than 80 per cent. of water present, fusel oil lowers the vapour-tension; at about 83 per cent. of water the influence of fusel oil is zero; with more dilute spirit fusel oil increases the vapour-tension. The raising or lowering of the vapour-tension is closely proportional to the percentage of impurity: 1 part of aldehyde or 10 parts of fusel oil in 10,000 of alcohol can be detected by this method. Even this degree of sensitiveness is, however, insufficient for the detection of the traces of impurity by which the value of a spirit may be greatly affected. Windisch's test for aldehyde is more delicate. A solution of aldehyde in 100,000 parts of alcohol shows a distinct green fluorescence when a few c.c. are treated with a small quantity of metaphenylenediamine hydrochloride and allowed to remain for an hour or two. The brown coloration attributed to aldehyde by Windisch is not characteristic. Fusel oil gives no colour with this reagent. M. J. S.

Terreil's Reaction for Testing the Colouring Matter of Wine. By L. WEIGERT (*Chem. Centr.*, 1888, 1592, from *Mitt. chem.-physiol. Versuchs-Stat., Klosterneuburg bei Wien.*, 5, 150).—The author considers the precipitation of the colouring matters with lead acetate of more value than with hot concentrated hydrochloric acid, and he further finds that the colour of the solution of the precipitate in alkalis is not green, but varies to all shades of brown, and also that the older the wine, the less trustworthy becomes the test.

J. W. L.

Tests for Archil, Cochineal, and Magenta in Wine. By P. PALMIERI and F. CASORIA (*Chem. Centr.*, 1888, 1594, from *Ann. Chim. Farm.*, 8, 141—143).—A strip of flannel is dipped into the wine previously heated to 70—80°, and to which aluminium acetate has been added. Pure wine colours it yellowish-brown; if archil is present it is coloured amaranth-red.

A still better test is to render the wine alkaline with barium hydroxide, and to boil the flannel in the filtrate. Pure wines do not colour it, but archil dyes it amaranth-red, which becomes violet when treated with ammonia.

The ether extract of natural wine becomes decolorised by ammonia, whereas in the presence of archil it is coloured violet.

Flannel dipped in hot dark-coloured wines, and afterwards treated with ammonia, becomes greenish if pure; cochineal causes a fast red, archil a violet, and magenta a fugitive red colour. J. W. L.

Reagents for Mercaptans. By G. DENIGÈS (*Compt. rend.*, **108**, 350—351).—A solution of isatin in sulphuric acid, so well known as a reagent for thiophen, may also be used as a reagent for mercaptans. When a small quantity of a 1 per cent. solution of isatin in sulphuric acid is mixed with a few c.c. of the strong acid and a small quantity of the mercaptan, or, better, its alcoholic solution, is added to the mixture, a green coloration is produced. Ethyl sulphide, sulphurous anhydride, and hydrogen sulphide do not give this reaction. A method of applying the test which is applicable to mixtures of mercaptans with other liquids, is to suspend a drop of the isatin solution at the end of a glass rod and introduce it into the upper part of the vessel containing the liquid. The coloration is obtained even when very small quantities of mercaptan are present, and if the coloured drop is transferred to a few c.c. of sulphuric acid and the process is repeated several times, a coloration of considerable intensity can be imparted to the acid. The reaction was obtained with methyl, ethyl, propyl, butyl, isobutyl, and amyl mercaptans, but is not given by the corresponding sulphides.

Aldehydes and higher alcohols interfere, and in presence of these compounds the liquid may be agitated for a short time with a solution of sodium or potassium hydroxide and then mixed with a small quantity of sodium nitroprusside. A red-violet coloration is produced. It is due to the action of the nitroprusside on a sodium or potassium derivative of the mercaptan and not to the formation of an alkaline sulphide, since the liquid gives no black precipitate with lead salts.

The alkyl sulphides and sulphurous anhydride do not give this

reaction. In presence of hydrogen sulphide or metallic sulphides, an alkaline solution of lead oxide should be used. Black lead sulphide is thrown down but does not interfere with the production of the coloration.
C. H. B.

Estimation of Raffinose in the Products of Beet-sugar Manufacture. By J. W. GUNNING (*Zeit. anal., Chem.*, 28, 45—57). —The German official method consists in determining the rotatory power (P) before and (J) after inversion by hydrochloric acid (compare Creydt, Abstr., 1887, 306), from which the percentages of saccharose and raffinose are calculated by the formulæ $S = \frac{0\cdot5188P - J}{0\cdot845}$ and $R = \frac{P - S}{1\cdot85}$, when 26·048 grams of substance has been taken. This method is, however, applicable only to mixtures containing 3 per cent. or more of raffinose, and fails altogether to detect such a quantity as 0·3 per cent. Scheibler's method (Abstr., 1887, 306) for the concentration of the raffinose, as also the later one of Lotman, based on the precipitation of the raffinose by lead acetate from the methyl alcohol solution, give results which are too high. This is due to the fact that absolute methyl alcohol dissolves not only the raffinose but also the greater part of the molasses constituents. On the other hand, lead acetate precipitates some saccharose as well as the raffinose from strong methyl alcohol, and although by the gradual addition of water the amount of the saccharose precipitated diminishes more rapidly than that of the raffinose, it is not possible to find a point at which complete separation takes place. In alcohol of 60—70 per cent., neither carbohydrate is precipitated by lead acetate. These properties furnish, however, a method for concentrating and determining mere traces of raffinose. 100 grams of the solid sugar is shaken for some time with 150 c.c. of commercial wood-spirit, to which a few drops of potash alum solution have been added. 100 c.c. of the solution is measured off and 40 c.c. of the alcohol is distilled off from it. To the residue, 20 c.c. of water is added, and then lead acetate, as long as a precipitate is produced. A little moist aluminium hydroxide is then added, with water to 100 c.c. After shaking, it is filtered and a portion polarised. 50 c.c. of the same filtrate is heated to remove the alcohol, made up again to 50 c.c., and inverted by adding 5 c.c. of hydrochloric acid of 36 per cent. and plunging for 10 minutes into water of 68°.

Products which do not readily give up their raffinose to dry alcohol, may be dissolved in the smallest quantity of hot water, neutralised with alum, mixed with the wood-spirit, cooled, and shaken for an hour with a little sugar powder. The greater part of the saccharose then crystallises out free from raffinose. The rotatory power of both sugars is somewhat greater in wood-spirit solution than in water. The following formula is for the solution in 60—70 per cent. wood-spirit, examined with a Laurent's polarimeter, for which 16·26 grams is the normal quantity.

$$16\cdot26\,\frac{(44 - 0\cdot5t)\cdot P - 102J}{158(44 - 0\cdot5t) + 102(75 + 0\cdot5t)} = \text{grams of raffinose in}$$
100 c.c.

M. J. S.

New Test for Thymol. By L. van Itallie (*Arch. Pharm.* [3], 27, 228).—To a solution containing thymol, some drops of potassium hydrate solution are added, and so much iodised potassium iodide solution that the solution becomes yellow, thus containing only a little free iodine. A beautiful red colour is obtained on gently warming; this gradually becomes more intense, but disappears after a time or on warming more strongly. The test detects about 1 : 20,000 of thymol in water. Other phenols examined did not give this coloration.

J. T.

Characteristic Reactions for Aldehyde. By H. Bornträger (*Chem. Centr.*, 1888, 1527, from *Chem. Tech. Zeit.*, **6**, 739).—Pure aldehyde is not changed by fuming nitric acid; the presence of alcohol, acetal, or amyl alcohol causes a very violent reaction immediately. Acetic acid also is not attacked by nitric acid. Other reactions of aldehyde are those with solutions of silver, and with magenta and sulphurous acid; with potassium iodide and starch-paste, it gives a blue coloration, and it bleaches indigo. Acetal may be distinguished from alcohol, aldehyde, amyl alcohol, and acetic acid by its reaction with magenta and sulphurous acid, which is immediately bleached. Acetic acid with this reagent gives a deep-red coloration only when heated, no reaction in the cold; it is thus distinguished from other substances with the exception of aldehyde. Acetic acid is reduced by sulphurous acid to aldehyde when heated, and the solution becomes red.

J. W. L.

Goldenberg's Method of Estimating Tartaric Acid. By H. Heidenhain (*Zeit. anal. Chem.*, **27**, 681—706).—The following points connected with this method were submitted to examination:—When potassium hydrogen tartrate is precipitated from an aqueous solution by alcohol, the amount remaining in solution is practically the same with all proportions between the limits of 2 vols. and 12 vols. of alcohol (95 per cent.) to 1 vol. of aqueous solution, being about 16 per cent. of the whole when the mixture remained in repose for 16 hours, but only 4 per cent. when the liquid was vigorously stirred for 5—15 minutes and filtered five minutes later. The percentage amount not precipitated was greater when the proportion of alcohol added exceeded 12 vols. The tartrate is quite insoluble in alcohol of 95 per cent. It begins to dissolve in alcohol of 90 per cent., and the solubility increases rapidly with further dilution. A neutral solution of potassium acetate decomposes potassium hydrogen tartrate, so that the addition of a small quantity of alcohol produces no precipitate, whilst a large quantity throws down normal tartrate. After addition of enough acetic acid to form potassium diacetate, alcohol throws down the potassium hydrogen tartrate, but not completely; a further quantity of acetic acid increases the amount of the precipitate, and a large excess is not injurious. As little as 0·75 milligram in 10 c.c. of aqueous solution containing potassium acetate and much free acetic acid will give a precipitate when mixed with 100 c.c. of alcohol. In this case also, stirring for five minutes is more efficient in promoting precipitation than 16 hours' repose.

Endeavouring to apply the above principles to the details of Goldenberg's method, the results still came out low. This appears to be due to the precipitation of a part of the tartaric acid as normal tartrate. It can be obviated by a double precipitation performed in the following manner:—1·88 grams of the potassium hydrogen tartrate and 1·25 grams of potassium carbonate are dissolved in 50 c.c. of water in a tared basin, 1·5 c.c. of glacial acetic acid is added, and the mixture is evaporated to 10 grams; 3 c.c. of acetic acid is now stirred in, 100 c.c. of alcohol added, and the mixture is again vigorously stirred for five minutes. After half an hour it is filtered and washed several times with strong alcohol by decantation, keeping the precipitate in the basin. The precipitate is now dissolved in hot water, 1·5 c.c. of acetic acid is added, and the solution is again evaporated, taking care to wash down the sides of the basin. When the contents are reduced to 10 grams, a further quantity of 1·5 c.c. of acetic acid is added, and the liquid is cooled; 10 vols. of alcohol are then added, together with 0·5 c.c. of a strong solution of potassium acetate. The mixture is stirred for five minutes, filtered after half an hour, washed with alcohol until the washings are perfectly neutral, and titrated. By this method 99·8—99·9 per cent. was obtained. With paper filters, it is difficult to avoid turbidity in the filtrate; Gooch's apparatus is more suitable. M. J. S.

Methods for Detecting the Adulteration of Butter. By C. BESANA (*Chem. Centr.*, 1888, 1597—1598, from *Staz. sperim. agric. ital.*, **15**, 47—86).—Having compared all the best known methods for the detection of butter adulterants, the author considers the Reichert-Meissl method as modified by Wollny the best, and that butter fat, 5 grams of which yield volatile acids equal to 27 c.c. or more N/10 alkali, may be considered pure; if the volatile acids equal less than 27 c.c. but more than 21·8 c.c. the butter should be further tested, whilst if the volatile acids equal less than 21·8 c.c., the butter may be undoubtedly condemned. J. W. L.

Detection of Cotton-seed Oil in Olive Oil. By E. HIRSCHSOHN and by J. BIEL (*Arch. Pharm.* [3], **27**, 32, from *Pharm. Zeit. Russ.*, **27**, 723).—3 to 5 c.c. of the oil to be tested is placed in a test-tube with 6 to 10 drops of a solution of 1 gram of crystallised gold chloride in 200 c.c. of chloroform; the tube is placed in boiling water, and heated for 20 minutes; no red coloration should appear. Experiments made with the following oils showed that they were indifferent to gold chloride under the above conditions: earth-nut, hempseed, linseed, poppy-seed, almond-kernel, mustard-seed, sesamé, and sunflower-seed, and wine-lees. Cotton-seed oil alone was found to take a coloration, rose-red at first, passing to cherry-red. On the other hand, cotton-seed oil is not detected equally well when mixed with other oils; the test does not succeed at all in drying oils, it succeeds very well in earth-nut, sesamé-seed, almond-kernel oils, &c., and best of all in olive oil, even 1 per cent. showing a raspberry-red colour in 20 minutes.

According to J. Biel (*Pharm. Zeit.*), 5 per cent. of cotton-seed oil in lard can be detected with certainty by gold chloride. J. T.

Cotton-seed Oil and Beef Fat in Lard. By J. A. Wilson (*Chem. News*, **59**, 99—100).—The author has noticed that cotton-seed oil, after keeping, loses its power of reducing silver nitrate, whether alone or mixed with lard; this is, therefore, an unsatisfactory test. He considers Hübl's reaction the best and most delicate, and has obtained the following results with it:—

	Iodine absorption per cent.	
	Maximum.	Minimum.
Cotton-seed oil	110·11	106·00
Linseed oil	149·10	148·07
Stettin rape oil	102·76	100·43
Castor oil	83·40	—
Palm oil	52·40	51·01
Olive oil	84·00	78·50
Neat's foot oil	70·70	70·00
Cocoanut oil	9·35	8·97
Lard	60·00	57·10
Beef fat	44·00	43·26
Mutton fat	46·19	45·18
Bone fat	49·58	46·27
Tallow	41·98	40·01

It is also observed that small percentages of cotton-seed oil can be detected by the action of sulphur chloride (compare Abstr., 1888, 1348; 1889, 318—320). D. A. L.

Adulteration of Lard. By G. Ambühl (*Chem. Zeit.*, **12**, 1521—1522; compare this vol., pp. 319—320).—Three tests are recommended as simple, rapid, and efficient, for the detection of cotton-seed oil in lard:—1. Determination of apparent gravity at 100° in the author's apparatus; lard indicates 60—62°, cotton-seed oil 68—70°, most American lards 64—65°. 2. The reduction of Bechi's silver nitrate solution. 3. Maumené's reaction; the author finds that lard gives a rise of 13—15°, cotton-seed oil 50—52°, American lards 30—35°, when 50 grams of fat are mixed with 10 c.c. of sulphuric acid at a constant temperature of 40°. D. A. L.

Oil of Anise. By J. C. Umney (*Pharm. J. Trans.* [3], **19**, 647—649).—The paper relates mainly to the solidifying point of commercial "oil of anise." This was formerly regarded as properly the product of *Pimpinella anisum*, but liable to adulteration with, or even to substitution by, the oil of star-anise, *Illicium anisatum*. The test that has been relied on was that the solidifying point of the former is between 10° and 15°, whilst the latter congeals at about 2°. The author contends, however, that when agitation is avoided, the oil from *Illicium anisatum* may, like water, be cooled below its normal solidifying point, and that it is this abnormal point which has been pre-

viously observed and recorded, whilst the true congealing temperature differs so little from that of the other oil that the test practically fails.
R. R.

A Delicate Reaction for Pine-wood Resin. By T. MORAWSKI (*Chem. Centr.*, 1888, 1630, from *Chem. Zeit.*, **12**, 1321—1322).—The resin is warmed gently with 5 c.c. of glacial acetic acid in a dry test-tube, and, after cooling, a drop of concentrated sulphuric acid is allowed to flow down the sides of the tube; as the liquids mix, a coloration varying from bright red to violet is produced. This reaction is recommended for testing the size of paper for resin.
J. W. L.

Detection of Antifebrin in Phenacetin. By J. SCHRÖDER (*Arch. Pharm.* [3], **27**, 226—228).—The two compounds are very similar in their physiological action, and probably phenacetin is frequently adulterated with the much cheaper antifebrin. Both compounds are partly decomposed in the organism; phenacetin yielding two non-poisonous compounds, phenetidine, $NH_2{\cdot}C_6H_4{\cdot}OEt$, and para-amidophenol, whilst antifebrin yields the poisonous compound aniline. Antifebrin when boiled with dilute nitric acid gives aniline and acetic acid, a reaction utilised as follows:—0·5 gram of phenacetin is boiled with about 6 c.c. of water, cooled, and filtered. The filtrate is boiled with potassium nitrite and dilute nitric acid; then a drop or two of Plugge's phenol test is added, and the solution is again boiled. If no red colour appears, antifebrin is either absent, or present in less quantity than 2 per cent. J. T.

Estimation of Methæmoglobin in the Presence of Oxyhæmoglobin. By E. LAMBLING (*Compt. rend. Soc. Biol.* [2], **5**, 473—475).—It has been stated (this vol., p. 531) that in the vacuum of an air-pump a certain amount of methæmoglobin may be formed in a solution of oxyhæmoglobin; the oxygen of this latter compound is not removable by such mechanical means. The oxygen is, however, removable by powerful reducing agents, such as ammonium sulphide and indigo-white, the reduction in each case stopping when hæmoglobin is formed. The following method is suggested as one to be adopted in determining the amount of methæmoglobin when mixed in solution with oxyhæmoglobin. A stream of hydrogen is passed through the mixture; this displaces the oxygen of oxyhæmoglobin and leaves the methæmoglobin intact: the liquid is then treated with indigo-white, and the quantity of indigo-blue formed measures the volume of oxygen yielded by the methæmoglobin. The quantity of methæmoglobin can be thus easily calculated, as the author finds, like Otto (*Pflüger's Archiv*, **31**, 245), that oxyhæmoglobin and methæmoglobin both yield the same percentage of loosely combined oxygen. W. D. H.

General and Physical Chemistry.

Calculation of Atomic Refractions for Sodium Light. By E. Conrady (*Zeit. physikal. Chem.*, **3**, 210—227).—The calculated values given are for hydrogen 1·051, chlorine 5·998, bromine 8·927, iodine 14·12. In the case of carbon, the author distinguishes between carbon which is directly united to carbon and hydrogen alone, and carbon which is also united to oxygen; the first has an atomic refraction of 2·501, the second 2·592. For oxygen, three values are given: the oxygen of an hydroxyl-group, 1·521, the oxygen of an ether, 1·683, and the oxygen of an aldehyde, 2·287. The value given for a double bond is 1·707.
H. C.

Contact-potential of a Metal and its Salts. By H. Pellat (*Compt. rend.*, **108**, 667—669).—When a metal such as mercury is allowed to run into an electrolyte, and the stream of metal is connected by a wire with a layer of the same metal at the bottom of the vessel, evidence of an electric current is generally obtained. If the metal which runs in is isolated, it acquires a constant potential after a very short time. The E.M.F. of a battery in which one element is a stream of running metal is quite different from that obtained with the same metal at rest. Experiments were made with mercury, and with liquid amalgams of copper and zinc, which in ordinary batteries, behave like copper or zinc alone. The normal difference of potential between a metal and a solution of one of its salts in contact with it is *nil*. The E.M.F. of a cell of the Daniell type is the sum of the difference of potential between the two liquids in contact and the difference of potential which would exist if the two metals were in contact. From this it follows that the difference of potential between two salts of the same acid, *plus* the difference of potential between the two metals in contact, is proportional to the quantity of heat developed by the substitution of the one metal for the other in the salt of the particular acid which is present.
C. H. B.

Electromotive Forces of Thin Layers of Hydrated Peroxides. By K. Schreber (*Ann. Phys. Chem.* [2], **36**, 662—671).—The question of the limiting thickness of thin layers below which they cease to show the ordinary properties of the material of which they are composed is one of considerable interest in molecular physics, and has attracted the attention of a considerable number of investigators (compare Rücker, Trans., 1888, 222). As would naturally be expected, the limiting values obtained in the case of any given substance vary considerably according to the nature of the phenomenon employed as a criterion.

For capillary phenomena, the limits according to Plateau, Quincke, and Reinold and Rücker, is about 50 micromillimetres, using the term micromillimetre to denote the millionth part of a millimetre.

For the phenomena of electromotive force, the limit according to Oberbeck is from 1 to 3 micromillimetres, whilst with respect to optical phenomena, such as the alterations in phase due to thin silver plates, Wiener (*Ann. Phys. Chem.* [2], **31**, 669) gives the limit at about 4 micromillimetres.

The substances selected by the author for his experiments were the hydrated peroxides of manganese, lead, and bismuth, deposited electrolytically, and his principal object was to determine whether the limit depended in any way on the complexity and constitution of the molecules. These substances, moreover, had the advantage over metals that they did not undergo any change through contact with air, and that it was easy to be sure of the layer being of uniform thickness by means of the uniformity in colour exhibited when this was the case. There was, moreover, no danger of solution taking place during the experiments, as happened in Oberbeck's investigations owing to the impossibility of attaining an absolutely neutral solution. In the case of the oxides of manganese and lead, the specific weights of the layers were found to be in very close agreement with those calculated from the current strength and the time, but in the case of oxide of bismuth the observed values were very much smaller than the calculated ones, and therefore in this case it was impossible to obtain any quantitative results. In the case of the oxide of manganese, the author found that, assuming the specific weight to be the same as that given by Wernecke, namely, 2·58, the limiting thickness below which the E.M.F. of polarisation ceased to be constant was about 250 micromillimetres. As long as the thickness exceeded this value, the E.M.F. was about 0·17 of a Daniell. As the layers became thinner than this limit, the E.M.F. was found to increase until it reached a maximum of 0·314 Daniell, with a thickness of 47 micromillimetres, assuming the chemical composition and density to remain unchanged. It then fell suddenly to 0·22 of a Daniell, and remained sensibly constant until the thickness diminished to about 2·3 micromillimetres.

The E.M.F. then again underwent a sudden fall, bringing it down to the value 0·04 of a Daniell, at which it remained constant. In the case of peroxide of lead, the author found that the E.M.F. of polarisation remained constantly equal to 0·26 of a Daniell until the limiting thickness of 71 micromillimetres was attained, after which the E.M.F., instead of increasing as in the former case, gradually diminished until the layer was only 40 micromillimetres in thickness, when its value was 0·22 of a Daniell. It then fell much more rapidly down to 0·17 of a Daniell at a thickness of 33 micromillimetres, where it remained constant until the thickness was diminished to 4·8 micromillimetres, it then again fell rapidly, and reached the value 0 for a thickness of 1·5 micromillimetre. From these results, it follows that the limiting thicknesses of the layers of hydrated peroxide of manganese and lead were 2·3 and 4·8 micromillimetres respectively, these being the thicknesses at which the last and most noteworthy fall in the E.M.F. was observed. These values are in close agreement with those obtained by Oberbeck, namely, 2·7 for zinc, 1·73 for cadmium, and 0·63 for copper, and they show that the compound molecules did not differ essentially in behaviour from elementary bodies. These compound molecules do not behave like elements when the thickness is somewhat greater, but the author considers that the variations in E.M.F. observed when the thickness of the layer was varied, were not due to the action of molecular forces proper, but to some variation in chemical composition which might very possibly consist in a change in the amount of water in the peroxide.

In conclusion, the author states that the thicker layers showed the well-known colours of thin plates, and up to a thickness of about 150 micromillimetres the colour was uniform over the whole plate, whilst with thicker layers bands were seen of a colour somewhat different to that of the rest. As the thickness was gradually diminished, the last colour observed was a faint yellow, and it ceased to be visible a little above the limiting thickness at which the last rapid fall in E.M.F. took place. G. W. T.

Initial Phase of Electrolysis. By N. Piltschikoff (*Compt. rend.*, **108**, 614—616).—When a current is passed between similar metallic electrodes immersed in a salt of the same metal, electrolysis takes place whatever the E.M.F. of the current, but if the cathode consists of a more electropositive metal, Lippmann has shown that electrolysis requires a certain minimum E.M.F. With gold and zinc electrodes in zinc sulphate, platinum and silver in silver nitrate or chloride, and platinum and copper in copper sulphate or nitrate, the minimum E.M.F. required is practically the same in all cases, and is 0·036 of the E.M.F. of a Daniell cell. The minimum E.M.F. required to produce visible electrolysis under these conditions is within certain limits independent of the nature of the acid in the salt, the concentration of the solution, and the relative heats of combination of the two metals, and their E.M.F. of contact. It is, however, greatly affected by the physical condition of the surface of the cathode. The phenomenon is conditioned by the relation between the molecular energy at the surface of the electrodes, or in other words by the relation between the energy required to separate *n* molecules of metal from the surface of the anode and that liberated by the deposition of *n* molecules on the surface of the cathode. The differences seem to be due to differences between the molecular pressures of the superficial layer of the anode and the superficial layer of the deposit on the cathode, and may alter as the layer of deposited metal on the cathode increases in thickness. C. H. B.

Electrolytic Polarisation by Metals. By N. Piltschikoff (*Compt. rend.*, **108**, 898—900). (Compare preceding Abstract.)

In a system consisting of a platinum cathode, a copper anode, and a solution of cupric sulphate, the opposing electromotive force with an anode of compact copper was equal to 0·038 of a Daniell cell, whilst with an anode of crystallised electrolytic copper it was 0·025 of a Daniell.

When the electromotive force tending to produce electrolysis is smaller than the opposing electromotive force, polarisation of course takes place; but the question arises whether the cathode is polarised by hydrogen or by the metal of the electrolyte.

With a platinum cathode and copper anode in a solution of cupric sulphate, the time required for the appearance of copper on the cathode becomes greater and greater as the electromotive force applied to the electrodes diminishes. With an electromotive force of 0·028 of a Daniell cell, half an hour is required to produce a visible deposit of copper, whilst with an electromotive force of 0·006 of a Daniell, 40 hours is required for the deposition of a minute speck of copper on the cathode. These numbers refer to an anode of compact copper; with an anode of crystalline electrolytic copper and an electromotive force of 0·0025 of a Daniell, there is a well-developed deposit of copper in 40 hours.

A gold cathode, a zinc anode, and a solution of zinc sulphate show similar phenomena, and hence the author concludes that one metal may be polarised by another. C. H. B.

Electrolytic Behaviour of Mica at High Temperatures. By W. H. SCHULTZE (*Ann. Phys. Chem.* [2], **36**, 655—662).—Warburg has shown (Abstr., 1884, 1241) that when a layer of glass between two mercury electrodes is traversed by an electric current, a badly conducting layer of silica is deposited on the side next the anode, the result of which is very soon to reduce the strength of the current to a minimum. The layer of silica acts exactly like the dielectric of a condenser, of which the mercury and the glass are the two coatings. The insulating power of glass at high temperatures, therefore, increases with increasing temperature, and at a sufficiently high temperature its surface conductivity is very much diminished. The object of the investigation described in the present paper was to make similar experiments with mica, which the author considered would be of value, owing to the various purposes for which this mineral is now employed.

The mica used in most of the experiments was of the kind known as muscovite, and the glass with which in some of the experiments the conductivity of the mica was compared, consisted either of white mirror-glass or thin watch-glass. Plates of mica split along the planes of cleavage were employed in all the experiments.

The method of observation was to heat the plates in an oven, and determine the change in conductivity by taking galvanometer readings at small intervals of time, the galvanometer being included in circuit with the plate.

The author found that as the temperature was gradually increased, the deflection of the galvanometer, both in the case of mica and of glass, gradually increased up to a maximum, and then diminished to considerably less than its initial value.

The results of the experiments show then that sheets of mica split along the plane of cleavage resemble glass in improving in conductivity as the temperature rises, and also in a maximum conductivity being obtained at a certain temperature, after which further increase in the temperature causes a diminution in conductivity, which appears to approach the value zero when the temperature becomes sufficiently high.

A comparison of the results obtained with mica and glass respectively showed that the mica was at all temperatures a better insulator than the glass. G. W. T.

Voltaic Energy of Electrolytes. By G. GORE (*Proc. Roy. Soc.*, **45**, 268).—Voltaic cells of unamalgamated zinc and platinum in distilled water are balanced through a sensitive galvanometer, and solutions of substances of known strength are added to one of the cells until the needle begins to move. As the energy required to move the needle is always the same, the quantities used represent the voltaic energy of the substances. A volta-tension series of electrolytes is drawn up commencing with chlorine (+1,282,000,000), and ending with potassium hydroxide (−270,985), and a mixture of salts, which gives −959,817. H. K. T.

Detection of Combining Proportions of Compounds by the Voltaic Balance. By G. GORE (*Proc. Roy. Soc.*, **45**, 265—267).—This method depends on the fact that "when substances chemically combine they lose some of their power of exciting a voltaic couple." Mixtures of two compounds are made in multiple proportions, and the amount of each of these solutions required to disturb the voltaic balance determined. That solution of which the largest amount is required represents the proportion for the constituents which gives the greatest amount of bound energy. With mixtures of potassium sulphate and nitrate, the least effect is observed when the constituents are in the proportion represented by the composition $K_2SO_4,2KNO_3$. In this way the existence in solution of a great number of molecular compounds was detected. In every case the constituents were united in equivalent proportions. The method may be used generally for the examination of the molecular constitution of chemical compounds in solution. Although, according to Thomsen, there is no thermochemical evidence of combination when molecular quantities of magnesium and potassium sulphates are dissolved, yet the voltaic balance gives unmistakable evidence of union. H. K. T.

Electrical Transport of Dissolved Salts. By A. CHASSY (*Compt. rend.*, **108**, 616—617).—The simplest case of electrical transport of a salt is presented by a non-electrolysed salt in a solution in which electrolysis is taking place, as, for example, zinc sulphate in a solution of copper sulphate. During electrolysis, the quantity of the non-electrolysed salt increases round the cathode and decreases round the anode. A porous diaphragm may conveniently be interposed but is not essential, and the phenomenon is quite distinct from electrical endosmose. In a mixture of the zinc and copper salts of the same acid, the quantity of zinc transported is independent of the concentration of the solution, and is a function of the relation between the masses of the two salts. The quantity of zinc transported increases in proportion as the ratio of copper to zinc decreases, and is also dependent on the intensity of the current and the nature of the acid in the salts.

When any two salts, for example, barium and sodium nitrates, are present in a constant ratio in a mixture of any number of salts whatever, the quantity of the two salts transported may vary in absolute value, but their ratio remains constant. C. H. B.

Determination of the Latent Heat of Fusion from the Reduction of the Freezing Point. By J. F. EYKMAN (*Zeit. physikal. Chem.*, **3**, 203—209).—The formula given by Van't Hoff (Abstr., 1888, 780) for the molecular reduction of the freezing point, $0·01976\ T^2/w$, where w is the latent heat of fusion of the solvent, may be employed for calculating the latent heat of fusion. Adopting Raoult's general law for the molecular reduction (Abstr., 1886, 763), we get $0·01976\ T^2/w = 0·62 \times$ mol. wt., or $w = 0·032\ T^2/$mol. wt. The results for the heats of fusion of a number of substances calculated from this formula do not agree with those obtained directly, however, and this is found to be due to the incorrectness of Raoult's general law. If the number for the molecular reduction obtained by experiment be employed a much better agreement is obtained, as the author shows for a number of substances for which he has determined the molecular reduction. H. C.

Specific Heat of Sea-water of different Specific Gravities. By THOULET and CHEVALLIER (*Compt. rend.*, **108**, 794—796).—500 c.c. of the sea-water, accurately measured, was placed in a platinum calorimeter, and a platinum flask containing 50 c.c. of heated water was introduced. The following results were obtained: other values obtained by interpolation are given in the original paper.

Specific gravity	1·0043	1·0073	1·0153	1·0176	1·0232
Specific heat	0·980	0·968	0·951	0·949	0·939

Specific gravity	1·0235	1·0290	1·0357	1·0463
Specific heat.........	0·938	0·927	0·921	0·903

If n is the number of molecules of water in which each molecule of salt is dissolved, and a and b are constants, then the value of γ, the specific heat, is given by the formula

$$\gamma = \frac{a + n}{b + n},$$

and this holds good if all the saline matter in the sea-water is taken as being sodium chloride.

If the mean sp. gr. of sea-water is taken as 1·0232 its mean specific heat is 0·939. The specific heat of air at constant pressure is 0·2374, and it follows that 1 c.c. of sea-water in cooling through 1° will raise the temperature of 3129 c.c. of air through 1°. These numbers explain the important climatic influence of the sea. C. H. B.

Heat of Formation of Antimony Hydride. By BERTHELOT and P. PETIT (*Compt. rend.*, **108**, 546—550).—Antimony hydride was prepared by the action of hydrochloric acid on an alloy of 1 part of antimony with 2 parts of zinc. The gas obtained, however, only contained a small percentage of the antimony compound. In order to determine the heat of formation, the gas was washed, and passed into a solution of potassium bromide containing free bromine and acidified with hydrochloric acid. Under these conditions, antimony pentabromide and hydrobromic acid are formed, thus:—$SbH_3 + 4Br_2 = SbBr_5 + 3HBr$. The antimony pentabromide remains in solution. A liquid of the same composition is obtained by dissolving antimony tribromide in a solution of potassium bromide which contains free bromine and hydrochloric acid. The mean of six experiments gave for the heat of formation of the gaseous hydride from solid antimony and gaseous hydrogen −84·8 cal., but the four most concordant experiments gave −85·5 cal. It is noteworthy that the heat of formation of cyanogen is −74·5 cal., and of acetylene −61·0 cal., and yet these compounds are very stable, whereas antimony hydride is very unstable.

The energy absorbed in the formation of the antimony hydride is furnished by the action of the hydrochloric acid on the zinc. In order to obtain the gas, the alloy must contain at least 5 atoms of zinc for each atom of antimony; an alloy of 1 atom of antimony with only 3 atoms of zinc gives no antimony hydride, as Cooke has previously shown.

The heats of formation of the four hydrides of the nitrogen-group are as follows:—NH_3, +12·2 cal.; PH_3, +11·6 cal.; AsH_3, −36·7 cal.; SbH_3, −84·5 cal.; and it is noteworthy that in the three last cases the differences between the heats of formation are almost the same as the differences between the molecular weights. C. H. B.

Thermochemistry of the Thionic Acids. By BERTHELOT (*Compt. rend.*, **108**, 773—779).—When treated with a solution of bromine in water or, better, in potassium bromide, the thionic acids are rapidly and completely converted into sulphates. In the case of dithionic acid, however, the reaction is too slow to be available for thermochemical purposes.

The following heats of dissolution were measured:—

Potassium trithionate, $K_2S_3O_6$ = −13·2 Cal.;
Sodium trithionate, $Na_2S_3O_6,3H_2O$, at 10° = −10·14 Cal.;
Sodium tetrathionate, $Na_2S_4O_6,2H_2O$, at 9·6° = −9·52 Cal.;
Potassium pentathionate, $K_2S_5O_6,1\frac{1}{2}H_2O$, at 9·5° = −13·12 Cal.

Assuming that the neutralisation of each of the thionic acids by sodium hydroxide develops the same amount of heat, the following results were obtained:—

$S_2 + O_2 + H_2O + Aq = H_2S_2O_3$ dil. develops +79·4 Cal.
$S_2 + O_5 + H_2O + Aq = H_2S_2O_6$ dil. ,, +206·8 ,,
$S_3 + O_5 + H_2O + Aq = H_2S_3O_6$ dil. ,, +211·4 ,,
$S_4 + O_5 + H_2O + Aq = H_2S_4O_6$ dil. ,, +205·2 ,,
$S_5 + O_5 + H_2O + Aq = H_2S_5O_6$ dil. ,, +215·8 ,,

Examination of these numbers shows that the heat developed per atom of oxygen is practically constant, the values being 39·70, 41·36, 42·28, 41·04, and 42·96 respectively. In other words, the combination of oxygen with sulphur develops practically the same quantity of heat, whatever the degree of condensation of the sulphur. In the formation of sulphurous, sulphuric, and persulphuric acids, the heat developed per atom of oxygen is 38·4, 47·0, and 36·2 Cals. respectively. The value is greatest, both absolutely and relatively, in the case of the most stable acid, and its magnitude is due to the formation of hydrates.

In the cases of selenium and tellurium, the values although close gradually decrease, and the same is true of arsenious and arsenic acids and the acids of phosphorus. These numbers afford considerable support to Dulong's law, that the heat of formation of oxy-acids is proportional to the quantity of oxygen which they contain.

From the heat of formation of thiosulphuric acid, it follows that its resolution into sulphurous acid and sulphur should be accompanied by the absorption of about −2·6 Cal. C. H. B.

Heats of Combustion of Metaldehyde, Erythrol, and Tricarballylic Acid. By LOUGUININE (*Compt. rend.*, **108**, 620—622).—The determinations were made with the calorimetric bomb:—

	Per gram.	Per gram-molecule. at constant volume.
Metaldehyde	6098·3	804976
Erythrol	4112·5	501725
Tricarballylic acid..	2940·9	517598

The heat of combustion of metaldehyde at constant pressure, 805790 cal., is practically the same as that of paraldehyde, 813200, and the difference may be attributed to the difference in their physical condition. The difference between the heats of combustion of citric and tricarballylic acids, 37498 cals., is practically identical with the difference in the case of lactic and propionic acids, 37400 cals.

C. H. B.

Dilatation and Compression of Carbonic Anhydride. By C. ANTOINE (*Compt. rend.*, **108**, 896—898).—A mathematical paper.

Relation between Osmotic Pressure, Reduction of the Freezing Point, and Electrical Conductivity. By J. H. VAN'T HOFF and L. T. REICHER (*Zeit. physikal. Chem.*, **3**, 198—202).—The amount of dissociation of different salts into their ions in dilute solutions is calculated from the osmotic pressure, reduction of the freezing point, and the conductivity, and the results compared. The numbers obtained by the three methods are in fair agreement in the cases of potassium and ammonium chlorides, calcium nitrate, and potassium ferrocyanide. With magnesium sulphate and the chlorides of calcium, lithium, strontium, and magnesium, the agreement is by no means a satisfactory one, but the cause of this exception to the general rule is not apparent. H. C.

Vapour-pressure of Aqueous Solutions. By G. TAMMANN (*Ann. Phys. Chem.* [2], **36**, 692—714).—In a former paper (Abstr., 1885, 862), the author endeavoured to show that the generalisations of Babo (*Ber. Beförd. Naturwiss. Freiburg*, 17—18) and Wüllner (*Ann. Phys. Chem.* **103**, 529; **105**, 185; **110**, 564) are, according to his measurements of the vapour-pressures of aqueous solutions, in contradiction to the requirements of the mechanical theory of heat. These laws, in fact, are only rough approximations. In a later paper (*Mém. l'Acad. St. Pétersbourg* [7], **35**), the author gave an investigation of the relation between the diminution in elasticity of the vapour, and the concentration of solutions, and arrived at the result that Wüllner's law of proportionality did not, in any one of the 185 cases investigated, represent the facts. When Wüllner enunciated his law, he observed that a good many substances only obey it when they are considered as hydrates in solution.

According to Babo's law, the vapour-pressure of the solution is at all temperatures proportionate to that of the solvent. In nearly all the cases investigated by the author, the results obtained are at variance with Babo's law, and he does not consider that the deviations are due to errors of observation, since they corresponded with the requirements of the theoretical law enunciated by Kirchhoff. The author discusses at some length the results obtained by a large number of previous investigators in the same field, and shows that in general they confirm his own measurements.

The paper contains an account of a large number of carefully made numerical observations, of which it will be sufficient to sum up the general results and compare them with the requirements of thermodynamics. According to Kirchhoff (*Ann. Phys. Chem.*, **103**, 200) the heat of formation of a solution can be determined when the relation between the temperature, the concentration, and the vapour-pressure is known. But this is, unfortunately, not of much assistance, as we do not know with any accuracy how the vapour-pressure and the heat of formation depend on the temperature.

Still, the experimental results can be compared with the theoretical ones so far as to show that there is a general agreement between them. Let $\mu = \mathrm{T} - \frac{1000\mathrm{T}_1}{\mathrm{T}m}$, where T and T_1 are the elasticities of the vapours given off by the solvent and the solution respectively, and m is the quantity of salt in 100 grams of water. Then, according to theory, the value of μ for dilute solutions in which no heat is evolved during solution would be independent of the temperature. Moreover, when the heat of formation of a saturated solution is positive, the value of μ will diminish as the temperature increases, and when the heat of formation is negative, it will increase with the temperature. According to Kirchhoff, the values of μ are independent of the temperature when the heat evolved during solution is infinitely small. This is confirmed by the following experimental results obtained by the author:—(1) The curves which represent the relation between μ and the concentration n of solutions of sulphuric acid and of iodide of cadmium at various temperatures intersect each other on the abscissa $n = 0$; (2) the isosmotic curves determined for dilute solutions at 17° coincide with the similar curves of equal vapour-pressure at 100°. Again, if Kirchhoff's proposition is true

Guldberg's results give $\frac{\nu}{\mu} = 104{\cdot}5$ for dilute solutions, where ν is the relative freezing point. The values obtained by the author are as given below:—

HCl.	$KCNS$.	KBr.	KI.	KNO_3.	$NaCl$.	$NaBr$.	NaI.	$NaNO_3$.	NH_4Cl.
105	100	119	108	97	101	104	109	106	113

NH_4CNS.	NH_4NO_3.	CH_3COONa.	$NaHO$.	KHO.	H_2SO_4.	K_2SO_4.	Na_2SO_4.
114	110	123	112	91	107	100	121

$(NH_4)_2SO_4$.	K_2CrO_4.	K_2CO_3.	Na_2CO_3.	$Mg(NO_3)_2$.	$CaCl_2$.	$Ca(NO_3)_2$.	$SrCl_2$.
123	91	113	97	117	118	98	115

$Sr(NO_3)_2$.	$BaCl_2$.	$Ba(NO_3)_2$.	CdI_2.	$Cd(NO_3)_2$.	$Zn(NO_3)_2$.	$NiCl_2$.	$Ni(NO_3)_2$.
100	102	88	102	120	119	120	111

$CoCl_2$.	$Pb(NO_3)_2$.	$MgSO_4$.	$MnSO_4$.	$ZnSO_4$.	$CuSO_4$.
128	92	114	105	119	115

In calculating these numbers, the values of ν were obtained by interpolation from the results given by Rüdorff (*Ann. Phys. Chem.*, **114**, 63; **116**, 55; **145**, 599) and de Coppet (*Ann. Chim. Phys.* [4], **23**, 366; **25**, 502; **26**, 29). These figures give 108·8 as the mean value of ν/μ, a result which is about 4 per cent. greater than the calculated value. This, however, appears to be explained by the fact that the observed freezing point of a solution is always lower than the actual freezing point, since the ice crystals separated from the solutions are always surrounded by layers of a high concentration. In order to see how far Kirchhoff's second requirement is fulfilled, we must know in what manner the heat of dissolution depends on the temperature. J. Thomsen (*Thermochemische Untersuchungen*, **1**, 8) has given a simple rule for this, namely:—If the heat of dissolution of an anhydrous salt is positive, it steadily increases with the temperature, but if it is negative it diminishes with increasing temperature and may ultimately become positive. Therefore, according to Kirchhoff, the values of μ should diminish as the temperature increases in the case of salts whose heat of dissolution is positive. This is in agreement with the author's measurements of vapour-pressures at different temperatures, and also with the results obtained by comparing the relative elasticity and the lowering of the freezing point. When the heat of formation is negative, the value of μ ought either to increase simply, or to first increase and then diminish as the temperature increases.

Examples of both these cases are to be found among the observations. Taking the whole series of 54 observations, 50 are in agreement with the theoretical requirements. G. W. T.

Solubility of Gases. By Woukoloff (*Compt. rend.*, **108**, 674—675).—The experiments which led Louguinine and Khanikoff and Wroblewski to the conclusion that the solution of carbonic anhydride in water does not take place in accordance with Dalton's law are inconclusive. Dalton's law only holds good when there is no chemical action between the dissolved substance and the solvent, and it is well known that carbonic anhydride and water form hydrates. Determinations of the solubility of carbonic anhydride in carbon bisulphide at various temperatures under low pressures show that although the law is not rigorously exact, the deviations are only small and are of the same order as the deviations from Boyle's law.

C. H. B.

Solubility of Salts. By H. LE CHATELIER (*Compt. rend.*, **108**, 565—567).—According to Roozeboom (*Rec. Trav. Chim.*, 8) the solubility of hydrated calcium chloride, $CaCl_2,6H_2O$, below its melting point is represented by a curve with two distinct branches which meet at the melting point of the hydrate. In other words, the same salt may have two different coefficients of solubility at the same temperature. The author finds, however, that if the curve is constructed on a sufficiently large scale it shows a well-marked angle, and hence consists really of two distinct curves which meet at the melting point of the hydrate, $CaCl_2,6H_2O$, one being the curve of solubility of the hydrate $CaCl_2,6H_2O$ in water, and the other the curve of the solubility of anhydrous calcium chloride in the hexahydrate. The author insists upon the fact that dissolution is always reciprocal.

C. H. B.

Rate of Transformation of Metaphosphoric Acid. By P. SABATIER (*Compt. rend.*, **108**, 738—741, and 804—806).—The author has previously found that the rate of change of metaphosphoric acid into orthophosphoric acid is proportional to the concentration of the solution (Abstr., 1888, 404), so that if x is the time and y the quantity of metaphosphoric acid present—

$$\frac{dy}{dx} = -y\frac{\log a}{\log e}.$$

a varies with the temperature and concentration, but within certain limits $\log a$ is proportional to the concentration, or, in other words, $\log a = mp + n$, p being the number of milligram-molecules per litre, whilst m and n vary with the temperature. The fact that hydration takes place more slowly the more dilute the solution indicates that combination with water is not the only change which takes place. There can be little doubt that the primary change is the resolution of a complex molecule, such as $3HPO_3$, the existence of which was assumed by Fleitmann and Henneberg. The final hydration of the simple molecule HPO_3 in all probability takes place with great rapidity.

With a given concentration, $\log a$ increases very rapidly with the temperature, and between 0° and 35° is almost proportional to the temperature. Between 0° and 40°, $\log a = 1{\cdot}125^t\,(0{\cdot}0000002p + 0{\cdot}00068)$.

The rate of change is increased by sulphuric acid, and still more by hydrochloric acid, but is reduced by acetic acid. If the acid is neutralised with potash, no change takes place at 0°, even after two months. At 43·5° the change takes place very slowly, but it becomes complete after prolonged boiling. When the acid is only partially saturated, the rate of change is slower than if all the acid were in the free state. If the free acid is assumed to change at the usual rate, the change of the salt takes place more rapidly than when the solution is neutral. This is doubtless due to the fact that the phosphoric acid formed from the free metaphosphoric acid liberates the acid from the potassium metaphosphate, and the liberated acid then undergoes hydration. In presence of excess of potash, the rate of change is greater than in neutral, but much less than in acid solutions. Between 0° and 20° it is very low indeed. C. H. B.

Unstable Equilibrium of Atoms. By E. PRINGSHEIM *physikal. Chem.*, 3, 145—158).—In substances which readily undergo sudden decomposition or isomeric change, the atoms are supposed to be in unstable equilibrium. The author points out that the heat developed in such cases is usually very large, and much greater than the energy required to bring about the decomposition. Hence if partial dissociation in the sense of the Clausius hypothesis is brought about by sudden raising of the temperature or some other disturbance, the heat generated serves to continue and complete the decomposition. H. C.

Lecture Experiments with Nitric Acid. By P. T. AUSTEN (*Amer. Chem. J.*, **11**, 172—177).—The author describes the phenomena attending the burning of charcoal, iron, sodium, sulphur, and other common combustibles in the vapour of nitric acid. G. T. M.

Inorganic Chemistry.

Hypochlorous Acid in Alkaline Solution. By P. T. AUSTEN (*Amer. Chem. J.*, **11**, 80—82).—When sodium hydrogen carbonate acts on a solution of bleaching powder, the following reactions take place:—(1.) $Ca(OCl)_2 + NaHCO_3 = CaCO_3 + NaOCl + HOCl$. (2.) $NaOCl + NaHCO_3 = Na_2CO_3 + HOCl$, or, expressed in one equation, $Ca(OCl)_2 + 2NaHCO_3 = CaCO_3 + 2HOCl + Na_2CO_3$. There is thus obtained a free mineral acid existing in a strongly alkaline solution. If the solution is heated, the hypochlorous acid decomposes with formation of hydrochloric acid and oxygen, the former of which liberates carbonic anhydride from the sodium carbonate, so that this gas and oxygen are evolved. A solution of sodium hypochlorite does not give off oxygen when boiled, unless carbonic anhydride has first been passed through it. A. G. B.

Atomic Weight of Oxygen. By W. A. NOYES (*Amer. Chem. J.*, **11**, 155—161; compare Abstr., 1888, 411, 647, and 649).—The method adopted was to pass a current of very nearly pure hydrogen into a glass bulb containing heated copper oxide, the water formed being condensed in a small tube leading from and sealed to the bulb. The increase in weight gave the hydrogen absorbed, and the subsequent decrease in weight, on exhausting the apparatus, the amount of water formed. The mean of six determinations was 15·886 ± 0·0028, which, if the correction made for nitrogen present in the hydrogen is omitted, is almost identical with the final mean (15·867) obtained by Cooke. On comparing this number with Keiser's results, the author, however, is led to the conclusion that some undiscovered source of constant error exists both in his and in Cooke's determinations. G. T. M.

Absorption of Nitrogen during Slow Oxidation. By BERTHELOT (*Compt. rend.*, **108**, 543—546).—When ether is slowly oxidised by air in presence of water, the product contains a small quantity of nitric acid. Very minute quantities of nitric acid are also formed during the slow oxidation of phosphorus. Experiments with terebenthene, mesitylene, benzaldehyde, and oleic acid were inconclusive, as also were experiments made with a view to ascertain whether ammonia is formed during the oxidation of iron by air in presence of water. C. H. B.

Action of Chlorine on Carbonic Anhydride. By R. LUCION (*Chem. Zeit.*, **13**, 32—33).—No reaction could be obtained, even at a red heat, by passing dry chlorine and carbonic anhydride through a heated porcelain tube. With chlorine and moist carbonic anhydride, however, hydrogen chloride is formed in the usual way. The author observed that 55 per cent. of the chlorine disappeared in this way when the carbonic anhydride was mixed with 8 per cent. of chlorine; when, however, the chlorine formed only 1 per cent. of the mixture, then only 11 per cent. of it was converted into hydrogen chloride. With air as a diluent, just the reverse took place, and the percentages of chlorine attacked were 14 in the first instance and 80 with the 1 per cent. mixture. D. A. L.

Vapour-density Determination of some Elements and Compounds at a White Heat. By H. BILTZ and V. MEYER (*Ber.*, **22**, 725—727).—The vapour-density determinations were made in an atmosphere of nitrogen, the apparatus being heated in a Perrot's furnace at 1650° to 1700°. The temperature was determined by means of an air thermometer having a bulb of Berlin porcelain; the air was collected in a gas burette divided into 200 c.c. A compensator with a second smaller gas burette eliminated the error caused by the lower temperature of the neck.

Bismuth has the density 11·893 and 10·125 between 1600° and 1700° ($Bi = 7·2$ and $Bi_2 = 14·4$). The bismuth molecule, like mercury, cadmium, and zinc, consists therefore probably of only one atom.

Phosphorus: density = 3·632 at 1484°, 3·226 at 1677° and 3·147° at 1708°.

Antimony: density = 10·743 at 1572° and 9·781 at 1640°.

Arsenic: density = 5·45 at 1714° and 5·371 at 1736°.

Thallium: density = 16·115 at 1636° and 14·248 at 1728°.

Arsenic and thallium would therefore seem to have diatomic molecules at these temperatures.

Cuprous chloride: density = 6·6035 at 1691° and 6·441; density required by the formula Cu_2Cl_2 = 6·825. There is therefore no dissociation at this high temperature.

Silver chloride did not completely volatilise at 1735°. The number 5·698 was obtained, AgCl = 4·965.

Sulphur, iodine, and mercury gave numbers corresponding with S_2, I, and Hg. N. H. M.

Molecular Weight of some Metaphosphates. By L. JAWEIN and A. THILLOT (*Ber.*, **22**, 654—655).—Molecular weight determinations of metaphosphates in aqueous solution were made by Raoult's method with the following results: Sodium trimetaphosphate 103, sodium hexametaphosphate 404 and 417, sodium dimetaphosphate (with 2 mols. H_2O) 121, ammonium dimetaphosphate 118. Considering that the mol. weight of sodium metaphosphate = 102, that of the tetrametaphosphate = 408, and that of ammonium metaphosphate 98, it may be concluded from the above results that the mol. weight of the trimetaphosphate is to that of the hexametaphosphate as 1 : 4, and not as 1 : 3, and that the di- and the tri-metaphosphates have the same mol. weight, corresponding with the formula MPO_3.

In the hope of being able to determine the molecular weights of metaphosphates by means of the alkyl salts, silver metaphosphates were heated with an excess of ethyl iodide. The ethyl salts are syrupy liquids of an agreeable odour, which thicken, but do not crystallise when cooled to −30°; they decompose when boiled.

N. H. M.

Sodium Zinc Oxides. By A. M. COMEY and C. L. JACKSON (*Amer. Chem. J.*, **11**, 145—154).—The authors have previously described (Abstr., 1888, 786) the preparation of two sodium zinc oxides, of which one melts below 100°, the other does not melt at 300°. The fusible sodium zinc oxide is now shown to have the formula $Zn_3Na_4H_2O_6 + 17H_2O$, which corresponds, except in water of crystallisation, with the ammonium zinc oxide described by Malaguti (*Compt. rend.*, **62**, 413). It melts at about 70°, is insoluble in ether, and rapidly absorbs carbonic anhydride from the air. When heated at 100°, it loses only 12 mols. H_2O. Water and, more slowly, alcohol decompose it with formation of a white powder consisting of zinc oxide mixed with a small quantity of zinc hydroxide, but these solvents are without action on it in presence of an excess of sodium hydroxide. The infusible sodium zinc oxide, which is formed in comparatively small quantities, has the formula $2NaO{\cdot}Zn{\cdot}OH + 7H_2O$, and corresponds with the potassium compound described by Fremy (*Compt. rend.*, **15**, 1106). It crystallises from a solution in dilute alcohol, containing an excess of sodium hydroxide, in conical, radiating groups of white needles, is decomposed by alcohol and by water, absorbs carbonic anhydride from the air, but less readily than the fusible compound, and does not lose all its water of crystallisation until heated above 200°. Attempts to obtain compounds of zinc oxide with ammonia, and of magnesium oxide with sodium hydroxide, were without success. G. T. M.

Formation of Cuprous Chloride and Bromide from Cupric Sulphate. By DENIGÈS (*Compt. rend.*, **108**, 567).—1 part of crystallised cupric sulphate, 1 part of metallic copper, and 2 parts of sodium chloride are boiled with 10 parts of water for four or five minutes. The solution rapidly becomes completely decolorised, and is then poured into 15 to 20 parts of water containing 1—2 per cent. of acetic acid. If the warmed solution is filtered and kept out of contact with the air, it deposits tetrahedra of cuprous chloride. This solution readily absorbs carbonic oxide and phosphine, and if mixed with ammonia until the precipitate redissolves, it can be used for the preparation of cuprous acetylide.

Similar results are obtained by using equivalent quantities of potassium or ammonium chloride. In the latter case, the cuprous chloride remains in solution, and this mode of preparation is especially applicable when the product is required for the absorption of carbonic oxide or phosphine.

Cuprous bromide can be obtained in a similar manner by using a quantity of alkaline bromide double that of the corresponding chloride. C. H. B.

Action of Ammonia on Mercurous Salts. By C. BARFOED (*J. pr. Chem.* [2], **39**, 201—229; compare this vol., p. 346).—The author has examined the precipitates formed by ammonia in solutions of mercurous salts, and comes to the following conclusions: (1.) Nearly half the mercury which the precipitate contains disappears as vapour when the precipitate is freely exposed to air, the exposure being under conditions which render chemical decomposition most improbable; the precipitate at the same time loses its dark colour. (2.) Exactly half the mercury exists in the precipitate uncombined, but does not all disappear as vapour, because a little of it acts on the rest of the precipitate, becoming fixed. (3.) The white or pale compound left after the mercury has evaporated is the same as that precipitated by ammonia in a solution of the corresponding mercuric salt. (4.) The dark precipitates are, therefore, not mercurous ammonium compounds, as heretofore stated, but mixtures of the mercuric ammonium compounds and mercury; thus, the precipitate produced from mercurous nitrate is $3Hg + 2(HgH_2N{\cdot}NO_3),HgO$, that from mercurous sulphate is $4Hg + (HgH_2N)_2SO_4,2HgO$, that from mercurous chloride is $Hg + HgH_2NCl$, and that from mercurous oxalate is $4Hg + (HgH_2N)_2C_2O_4,2HgO$. (5.) The black precipitate obtained by Kane from ammonia and mercurous nitrate is also a mixture containing mercury, but not the same as that given above. (6.) Rose's ammoniacal mercurous chloride, obtained from anhydrous ammonia and mercurous chloride, is the same as that given above, but contains ammonium chloride in addition. A. G. B.

chloric acid, precipitated with ammonium carbonate, and weighed as a control to a separate estimation. The solution is nearly neutralised with nitric acid, mixed with calcium chloride, boiled, and the precipitate filtered, washed, dried, and ignited. It is treated with acetic acid, dried, extracted with water, and the calcium fluoride washed, dried, and weighed. D. A. L.

Aluminium Subfluoride. By W. DIEHL (*Chem. Zeit.*, **13**, 162).—Referring to Hampe's experiments (preceding Abstract), it is suggested that the apparent formation of aluminium subfloride is possibly merely due to the presence of some alumina formed during the fusion. The loss of aluminium observed in the electrolysis of cryolite (preceding page) is explained by Beketoff's experiments, where it was observed that, at very high temperatures, aluminium reacts with the alkaline and alkaline earthy fluorides, setting free the metal from them with the simultaneous formation of aluminium fluoride.

Hampe (*Chem. Zeit.*, **13**, 162—163) refutes these statements so far as they affect his experiments. D. A. L.

Metallic Sulphides. By A. GAUTIER and L. HALLOPEAU (*Compt. rend.*, **108**, 806—809).—The substance, which in these experiments was either a metal or a silicate, was supported on a dish of gas-carbon or graphite and placed in a glazed porcelain tube. After all the air had been expelled by hydrogen, the substance was heated at 1300—1400° in a current of the vapour of carefully dried carbon bisulphide for five or six hours, and was allowed to cool in the bisulphide vapour. The sulphide formed usually remains in the dish, sometimes covered with a layer of the carbide. Carbon, sulphur, and a reddish-yellow substance which may be carbon monosulphide, are carried forward by the vapour. Any silica which is present in the free state or in a silicate is converted into silicon sulphide, which crystallises in the cooler parts of the tube.

Soft iron yields the sulphide Fe_4S_3 as a crystalline mass of sp. gr. 6·957 at 0°; hardness 3·8°. It does not alter when exposed to air, is oxidised with difficulty, but dissolves in dilute acids with evolution of hydrogen sulphide and hydrogen. It is crystalline and homogeneous, does not dissolve in ammonium acetate or chloride, and does not evolve hydrogen sulphide with boric acid solution. It is therefore not a mixture of iron and ferrous sulphide, but must be regarded as a distinct sulphide intermediate between F_4S_2 and FeS.

Manganese yields manganous sulphide, MnS, no subsulphide being formed even in presence of excess of the metal. The sulphide is olive-green with a crystalline fracture, and does not decompose water even on boiling. A carbide is formed at the same time which has the composition MnC_2, and crystallises in small, brilliant, black octahedra.

If rhodanite, $MnSiO_3$, is heated in the bisulphide vapour at a very bright red heat, it yields a sulphide, Mn_3S_4, which has a semi-metallic appearance, decomposes water slowly in the cold and rapidly on heating, with formation of hydrogen sulphide and manganese hydroxides, and dissolves very rapidly in dilute acids. C. H. B.

Ochres, Siennas, and Umbers. By G. H. HURST (*Chem. News*, **59**, 172—174).—The author gives analyses of 14 samples of ochres, siennas, and umbers, and finds they generally contain water, a little organic matter, lime, silica, alumina, and ferric oxide; in some sulphuric acid is also found, in others both barium and sulphuric acid. Ochres contain no manganese, siennas a small proportion, umbers a larger quantity. Two samples of ochre, one Irish, one Welsh, contained a little copper. An analysis of Terre Verte is also given.

D. A. L.

Peroxides of Nickel and Cobalt: Estimation of Nickel and Cobalt. By A. CARNOT (*Compt. rend.*, **108**, 610—612).—The brown oxide obtained by precipitating a boiling solution of a cobalt salt with potassium hydroxide and hydrogen peroxide has exactly the composition of a sesquioxide, Co_2O_3. Under the same conditions, nickel salts yield only nickelous hydroxide, $Ni(OH)_2$. When, however, nickel salts are oxidised with a hypochlorite, or with bromine in presence of potassium hydroxide, they yield a pure sesquioxide, Ni_2O_3. Both metals can be estimated accurately by treating the sesquioxide with hydrochloric acid and potassium iodide, and determining the amount of iodine liberated.

The black cobalt oxide obtained by oxidising cobalt salts with sodium hypochlorite, bromine, or iodine, in presence of potassium hydroxide, always contains more oxygen than the sesquioxide. If the hypochlorite is used, each atom of available oxygen corresponds with only 1·67 atoms of cobalt, and if bromine is used, with only 1·6 atoms.

For accurate estimations of cobalt, hydrogen peroxide must be used, and for estimation of nickel, bromine or a hypochlorite. Cobalt can be estimated in presence of nickel, since the latter is not oxidised by hydrogen peroxide. Boiling the liquid with ammonia, with a view to decompose any traces of nickel sesquioxide that might be formed, has no influence on the results.

C. H. B.

Oxy-haloid Derivatives of Chromium. By S. G. RAWSON (*Chem. News*, **59**, 184—185).—The author has repeated Girard's experiments, but could not obtain iodochromic acid by distilling sulphuric acid with potassium dichromate and potassium iodide, the distillate consisting of hydriodic acid, iodine, and traces of sulphuric and sulphurous acids. Many unsuccessful attempts were made to prepare iodo- and bromo-chromic acids by the action of chlorochromic acid on ethyl iodide and calcium iodide and bromide, of hydriodic acid on chromic acid in presence of zinc chloride, and by other reactions. The author believes there were some indications of the formation of a cyanochromic acid as a product of the action of chlorochromic acid on silver or mercuric cyanide.

Incidentally it is noted that the green tinge imparted to a borax bead by 0·000005 gram of chromium may be recognised by comparison with a pure borax bead.

D. A. L.

Nitroso-compounds of Ruthenium. By A. JOLY (*Compt. rend.*, **108**, 854—857).—When brown ruthenium sesquichloride is treated with a large excess of nitric acid, it yields a red nitrate, and when this compound is treated with successive quantities of hydrochloric acid and boiled for a long time, it yields a pale crimson solution of a chloride. If this solution is evaporated at 120°, it leaves a brick-red, crystalline mass of the composition $RuCl_3 \cdot NO + H_2O$. This compound is only very slightly soluble in cold water, but dissolves more readily in hot water, from which it crystallises with 5 mols. H_2O in strongly dichroic, flattened, triclinic prisms, measurements of the angles of which are given in the original paper. The crystals effloresce rapidly in dry air; they lose 2 mols. H_2O in a dry vacuum or at 100°, and an additional 2 mols. between 120° and 150°, but the last molecule of water is only expelled at a temperature at which the salt begins to decompose. When heated at 440° in carbonic anhydride or in a vacuum, the monohydrate $RuCl_3 \cdot NO + H_2O$ decomposes rapidly with evolution of nitrogen oxides, and leaves a residue of ruthenium sesquichloride and the dioxide. It is also reduced by hydrogen at a comparatively very low temperature with incandescence and sublimation of ammonium chloride.

When the hydrochloric acid solution of this compound is concentrated in a vacuum, it forms a non-crystallisable syrup, and when this is heated there is rapid evolution of hydrogen chloride, and the monohydrated salt is obtained. It is possible that a definite hydrochloride exists, but this has not yet been isolated.

Solutions of the nitroso-sesquichloride or of the double alkaline salts are not precipitated by alkalis in the cold, but if the solutions are mixed with sufficient alkaline hydroxide or carbonate to combine with three atoms of chlorine, and are then boiled, a pale brown gelatinous precipitate is formed, and the supernatant liquid is neutral. After drying at 150°, it forms a black mass with a vitreous lustre. It has the composition $Ru_2O_3(NO)_2 + 2H_2O$, and is not decomposed by heat at temperatures below 300°. If heated at 360° in a current of carbonic anhydride, it slowly decomposes, and yields a black, graphitoidal oxide, Ru_4O_9, identical with the oxide obtained by the action of hot water on ruthenium peroxide (Abstr., 1888, 560). Above 440°, it decomposes explosively with incandescence and evolution of nitrogen oxides. It is reduced by hydrogen below 100° with incandescence and evolution of ammonia. The precipitated oxide dissolves in excess of the alkaline hydroxides or carbonates, but is reprecipitated on neutralising the solution; ammonia or ammonium carbonate converts it into an amine. The nitroso-oxide dissolves readily in many acids, forming definite salts. With hydrobromic and hydriodic acids, it forms a bromide and iodide which are analogous to the nitrosochloride, and like it form double salts with the corresponding haloid salts of the alkali metals. C. H. B.

Mineralogical Chemistry.

Peridotite of Elliott Co., Kentucky. By J. S. DILLER (*Amer. J. Sci.*, **37**, 219—220).—G. H. Williams (Abstr., 1888, 120) recently identified perofskite in the serpentine of Syracuse, New York, and suggested that the yellowish grains, that were supposed to be anatase in the peridotite of Elliott Co. (*U.S. Geol. Surv. Bull.*, No. 38), may be the same material. This view is supported by the results of an analysis of these grains, which clearly demonstrates that they are composed essentially of titanic anhydride and lime. B. H. B.

Pseudo-brookite. By G. LATTERMANN (*Jahrb. f. Min.*, 1889, i, Ref., 202—203, from *Min. petr. Mitth.*, **9**, 47).—In a variety of the rock of Katzenbuckel, the author has found pseudobrookite in sufficient quantity to enable him to investigate its properties. The minute crystals are limited by macro- and brachy-pinacoids, and by a doma $\frac{1}{3}\bar{P}\infty$. Occasionally ∞P also occurs. The mean of two analyses of the mineral gave the following results :—

TiO_2.	Fe_2O_3.	MgO.	Total.
46·79	48·64	4·53	99·96

B. H. B.

Kroehnkite. By L. DARAPSKY (*Jahrb. f. Min.*, 1889, i, Mem., 192—195).—Kroehnkite is a double sulphate of copper and sodium, which has hitherto been found only in the desert of Atacama. It is named after B. Kröhnke, who first described and analysed it in 1875. The author has found some fine crystals of this mineral in the National Museum of Santiago de Chile. The crystals are monoclinic, with the axial ratio $a : b : c = 1 : 2·112 : 0·649$; $\beta = 64° 8'$. The mineral has a hardness of 2·5, and a sp. gr. of 1·98. The analytical results are in accord with those obtained by Kröhnke, the formula of the mineral being $CuSO_4 + Na_2SO_4 + 2H_2O$. A salt of the same composition was prepared artificially by Graham. B. H. B.

Formation of Deposits of Nitrates. By A. MÜNTZ and V. MARCANO (*Compt. rend.*, **108**, 900—902).—The authors have previously attributed the formation of the deposits of nitrates in South America to the enormous deposits of the excrement of birds, bats, &c., which occur in the immense caverns in the Cordilleras (Abstr., 1885, 1042). The formation of deposits of nitrates can in fact actually be watched.

In many large caverns there are no remains of birds, but the soil is charged with nitrates and is found to contain enormous quantities of the bones of mammals. These bones are very friable, and consist of calcium phosphate with very small quantities of organic matter. Calcium carbonate is absent, and has indeed been converted into calcium nitrate, which is found in the earth by which the bones are surrounded. Bone caverns are numerous in Venezuela, not only in the littoral mountains but also on the flanks of the Cordillera of the

Andes. In some cases the deposit exceeds 10 metres in thickness, and the earth is highly charged with the nitric ferment. The quantity of calcium nitrate present varies from 4 to 30 per cent., and the quantity of calcium phosphate from 5 to 60 per cent.

These observations confirm the authors' previous conclusions as to the origin of the nitrates (*loc. cit.*). C. H. B.

Gehlenite in a Furnace Slag. By J. S. DILLER (*Amer. J. Sci.*, **37**, 220).—Numerous square prisms of gehlenite occur in a furnace slag found near McVille, Armstrong, Pennsylvania. Under the microscope, the isotropic square sections are readily found to be uniaxial and negative. Spherical, liquid, and rod-like inclusions are numerous. Cleavage lines are not conspicuous. The easy gelatinisation of the mineral in hydrochloric acid, and its difficult fusibility, distinguish it from similar minerals. Gehlenite has not previously been reported as occurring in the United States. B. H. B.

Note.—A rare blast furnace slag of the composition of gehlenite, from the Almond Ironworks, Falkirk, N.B., has been described by H. Bauerman (*J. Iron and Steel Inst.*, 1886, 88). B. H. B.

Dumortierite from Harlem, New York, and Clip, Arizona. By J. S. DILLER and J. E. WHITFIELD (*Amer. J. Sci.*, **37**, 216—219).—A description by R. B. Riggs (Abstr., 1888, 351) of the so-called Harlem indicolite, which was regarded as a new borosilicate, led to E. S. Dana identifying the mineral as dumortierite. The physical properties of the Harlem dumortierite agree closely with those mentioned by Bertrand, Gonnard, and Damour. Crystals are very rare, but the mineral is evidently rhombic. Its hardness is 7, and its sp. gr. is 3·265. The mineral occurs at Harlem in the pegmatoid portions of a biotite gneiss. These portions are composed of quartz, orthoclase, some plagioclase, and tourmaline. The tourmaline, whose presence was not at first recognised, is so intimately associated with the dumortierite that they cannot be easily separated. An analysis of 0·217 gram of dumortierite separated from the tourmaline, gave 31·44 per cent. of silica, 68·91 of per cent. of alumina, and a trace of beryllia. An analysis of a large quantity of material from Clip, Yuma Co., Arizona, gave the following results:—

SiO_2.	Al_2O_3.	MgO.	B_2O_3.	P_2O_5.	H_2O.	Total.
27·99	64·49	trace	4·95	0·20	1·72	99·35

In the material analysed, the only associated mineral was quartz, which was decomposed by hydrofluoric acid, dumortierite not being acted on by that acid. The analytical results indicate that dumortierite is not a simple aluminium silicate as stated by Damour, but corresponds approximately with the formula $3Al_8Si_3O_{18}AlB_2O_6,2H_2O$. B. H. B.

Eclogite from Frankenstein in Silesia. By H. TRAUBE (*Jahrb. f. Min.*, 1889, i, Mem., 195—200).—The group of mountains, rising to the south-west of Frankenstein, consists of gabbro, amphibolite, and serpentine. In the south-west flank of this chain, the author noted the occurrence of garnet-bearing gabbro, which he described in 1884. He now supplements his former memoir by a description of an occurrence of eclogite in the serpentine at the same locality. The eclogite occurs in two varieties, coarse-grained and fine-grained. The former variety consists of an augitic constituent and garnet. Of these two minerals, the author gives a number of analyses. The augite is best described as an omphacite resembling diallage. In the fine-grained eclogite, the size of the constituents is so reduced that it is frequently impossible to distinguish the two minerals with the naked eye. The garnet encloses serpentine and zoisite as well as omphacite. Quartz is absent, and zircon and cyanite, two minerals that are of general occurrence as accessory constituents of eclogite, could not be detected. B. H. B.

Solubility of Minerals in Sea-water. By J. Thoulet (*Compt. rend.*, **108**, 753—755).—The finely powdered minerals were dried at 125°, and were then enclosed in flasks with filtered sea-water, the flasks and their contents being repeatedly agitated. After a week, the water was drawn off and replaced by fresh sea-water, the treatment being continued for seven weeks. At the end of this time, the sea-water was replaced by distilled water, and the treatment continued for another seven weeks. A similar set of experiments with distilled water only was conducted simultaneously for seven weeks. At the end of the experiment, the minerals were washed, dried, and weighed. The following table gives the weight of mineral dissolved per gram of original substance, the quantity of sea-water used being about 5 litres in each case, and the weight of mineral taken for each experiment varying from 3 to 6 grams :—

	Obsidian.	Pumice.	Amphibole.	Orthoclase.
Sea-water......	−0·0001	−0·0036	−0·0015	+0·0001
Distilled water..	−0·0000	−0·0044	−0·0011	−0·0015

	Marble.	Shells.	Coral.
Sea-water	−0·0165	−0·0206	−0·0264
Distilled water	−0·0166	−0·0195	−0·0267

The quantity dissolved by sea-water is almost always slightly less than that dissolved by distilled water, a result which is probably due to the alkaline reaction and the absence of carbonic anhydride. With a view to eliminate the influence of a possible growth of algæ on the surfaces of some of the minerals, it will be necessary to repeat the experiments in the dark. C. H. B.

Waters of the Yellowstone National Park. By F. A. Gooch and J. E. Whitfield (*Amer. J. Sci.*, **37**, 234, from *Bull. U.S. Geol. Surv.*, No. 47).—The authors give careful analyses of 43 samples of the geyser waters. The results are of interest because of the evidence they appear to afford that the silica present in the siliceous waters is mostly in the state of dissolved silica, and not in that of an alkaline silicate. The silica constituted 26·54 per cent. of the total material in solution in the water of the Old Faithful Geyser, 27·62 per cent. in Giantess, 25·12 per cent. in the Beehive, and 18·15 per cent. in the Grotto. Of the other ingredients, the analyses give 1·43 to 1·75 per cent. of boric acid, 16·89 to 39·22 per cent. of chlorine, and 15 to 28 per cent. of sodium, in 100 parts of the total solid material.

B. H. B.

Organic Chemistry.

Dimolecular Methyl Cyanide. By R. HOLTZWART (*J. pr. Chem.* [2], **39**, 230—245).—The formation of this substance (already described, this vol., p. 113) takes place as follows:—(1) $Na_2 + 2CH_3{\cdot}CN = NaCN + CH_4 + CH_2Na{\cdot}CN$; (2) $CH_2Na{\cdot}CN + CH_3{\cdot}CN = C_4H_5NaN_2$; (3) $C_4H_5NaN_2 + H_2O = C_4H_6N_2 + NaOH$. Its constitution is most likely $NH{:}CMe{\cdot}CH_2{\cdot}CN$, *imidoacetylmethyl cyanide*, but some of its reactions are in accord with the view that it is *β-amidocrotonitrile*, $NH_2{\cdot}CMe{:}CH{\cdot}CN$. When it is reduced by sodium in alcoholic solution, ethylamine and ammonia are evolved.

The substance $C_8H_9N_3$, obtained by the action of water on the compound of imidoacetylmethyl cyanide with acetic chloride (this vol., p. 114), crystallises in beautiful, long, white needles melting at 222—223°.

When imidoacetylmethyl cyanide is warmed with 25 per cent. hydrochloric acid, half of its nitrogen is converted into ammonium chloride, and if the product is extracted with ether, a small quantity of oil is obtained; this is cyanacetone, $COMe{\cdot}CH_2{\cdot}CN$, for it gives a condensation product, $C_{10}H_{11}N_3$, with phenylhydrazine; this crystallises in white, sparingly soluble needles melting at 96—97°, and is unstable in air (or on exposure to light?). The cyanacetone gradually solidifies to a glassy mass, which carbonises above 230°.

When imidoacetylmethyl cyanide is boiled with water, ammonia, cyanacetone, and the substance $C_8H_8N_2O$ (this vol., p. 114), are obtained. When the latter is treated with phosphorus pentachloride (equal mols.), a crystalline substance of peculiar odour, and melting at 174—175°, is obtained; it cannot be quite freed from chlorine by recrystallisation from petroleum, but when recrystallised from water it has the formula $C_8H_6N_2$.

Imidobenzoylmethyl cyanide, $NH{:}CPh{\cdot}CH_2{\cdot}CN$, or *β-amidocinnamonitrile*, $NH_2{\cdot}CPh{:}CH{\cdot}CN$, is obtained by acting on a mixture of methyl cyanide (2 mols.) and phenyl cyanide (1 mol.) in ether, with sodium (2 mols.), and treating the reddish-grey sodium compound formed with water. It crystallises in small, white needles melting at 86°.

Cyanmethine may be synthesised by heating a mixture of the sodium compound, $C_4H_5NaN_2$, and sodium cyanide, in a sealed tube at 140°.

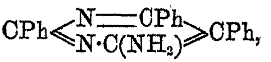
A. G. B.

Polymerides of Nitriles. By R. WACHE (*J. pr. Chem.* [2], **39**, 245—261).—To prepare *dimolecular propyl cyanide*, or *imidobutyrylpropyl cyanide*, $\mathrm{NH{:}CPr^{\alpha}{\cdot}C_3H_6{\cdot}CN}$, sodium (4 grams) is added to propyl cyanide (20 grams) dissolved in ether; propane is evolved, and a granular sodium-derivative separates; this is decomposed by water; the resulting oil is dissolved in ether and distilled, when the imido-compound distils over at 279—280° (uncorr.) as a thick, yellowish oil. Its formation is analogous to that of dimolecular methyl cyanide (preceding Abstract).

By heating the sodium-derivative with propyl cyanide at 180° in a sealed tube, cyanopropine (Abstr., 1888, 800) is obtained; with ethyl cyanide under the same circumstances *cyandiethylpropine*, or *amidotriethylmetadiazine*, $\mathrm{CEt}\left<\begin{matrix}\mathrm{N{=\!=}CEt}\\ \mathrm{N{\cdot}C(NH_2)}\end{matrix}\right>\mathrm{CEt}$, is obtained; this separates from hot alcohol in monoclinic crystals, which are easily soluble in alcohol and in ether, sparingly in water, and melt at 183—184°. When heated with concentrated hydrochloric acid at 170°, *hydroxytriethylmetadiazine*, $\mathrm{C_{10}H_{15}N_2(OH)}$, is obtained; it crystallises in white, silky needles melting at 144°; its *silver derivative*, $\mathrm{C_{10}H_{15}AgN_2O}$, is described.

Imidocaproylcapronitrile, $\mathrm{C_5H_{11}{\cdot}C(NH){\cdot}C_5H_{10}{\cdot}CN}$, is prepared from amyl cyanide and sodium, as described above; it is a yellow, syrupy oil boiling at 245° at 20 mm. pressure. When heated with concentrated hydrochloric acid at 150°, it is converted into ammonium chloride and di-isoamyl ketone.

When benzyl cyanide is heated with sodium in ether, a red precipitate is produced, which is presumably the sodium-derivative of dimolecular benzyl cyanide, but the latter cannot be isolated. If the precipitate is heated with phenyl cyanide for five hours at 170—180°, and then digested with ether, *amidotriphenyl metadiazine*,



$$\mathrm{CPh}\left<\begin{matrix}\mathrm{N{=\!=}CPh}\\ \mathrm{N{\cdot}C(NH_2)}\end{matrix}\right>\mathrm{CPh},$$

is extracted; this base crystallises in slender, lustrous aggregates of needles, melting at 175°; the *hydrochloride*, $\mathrm{C_{22}H_{17}N_3,HCl}$, has been obtained. The *hydroxy*-derivative, $\mathrm{C_{22}H_{15}N_2{\cdot}OH}$, formed in the usual way, crystallises in felted needles melting above 340°.

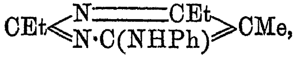
By substituting benzyl cyanide for phenyl cyanide in the above reaction, treating the residue left by ether with water, and the residue left by this with alcohol, *cyanbenzyline*, or *amidophenyldibenzylmetadiazine*, $\mathrm{C_7H_7{\cdot}C}\left<\begin{matrix}\mathrm{N{:}C(C_7H_7)}\\ \mathrm{N{\cdot}C(NH_2)}\end{matrix}\right>\mathrm{CPh}$, is obtained in white needles melting at 106° (uncorr.); it is also formed when benzyl cyanide is heated with sodium ethoxide. The *hydrochloride* and *platinochloride*, $\mathrm{(C_{24}H_{21}N_3)_2,H_2PtCl_6}$, are described.

The *hydroxy*-derivative, $\mathrm{C_{24}H_{19}N_2{\cdot}OH}$, crystallises in white, felted needles melting at 180° (uncorr.); it is obtained either by heating cyanbenzyline with concentrated hydrochloric acid, or by passing nitrous anhydride through its acetic acid solution. The *acetyl*-derivative melts at 84—85° (uncorr.).

A (presumably) dimolecular benzoyl cyanide is obtained by warming benzoyl cyanide with sodium in ether; it crystallises in needles melting at 95° (uncorr.). A. G. B.

Cyanethine and its Derivatives. By E. v. MEYER (*J. pr. Chem.* [2], **39**, 262—283).—The author formulates cyanethine and its known analogues as amidoalkylmetadiazines (this vol., p. 577), and discusses the evidence in favour of this view. Cyanethine yields ammonia and methyldiethylmetadiazine (cyanoconiine, Abstr., 1883, 352) when reduced by zinc; ammonia, propaldehyde, and an oil, when reduced with sodium and alcohol; and ammonia, propaldehyde, and an oil, $(C_9H_{16}N)_2O$, when reduced with sodium amalgam in acid solution.

Phenylamidomethyldiethylmetadiazine (*phenylcyanethine*),



$$\mathrm{CEt}<\begin{matrix}\mathrm{N}{=\!=\!=\!=}\mathrm{CEt}\\ \mathrm{N{\cdot}C(NHPh)}\end{matrix}>\mathrm{CMe},$$

obtained by heating chloromethyldiethylmetadiazine with aniline and a little alcohol at 220°, crystallises in slender needles, melts at 99°, and is soluble in organic solvents. The *hydrochloride* and *platinochloride* are described.

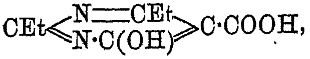
Phthalylcyanethine, $C_9H_{13}N_2{\cdot}N{:}C_2O_2{:}C_6H_4$, is formed when phthalic anhydride and cyanethine (equal mols.) are heated together; it is extracted from the mass by ether, from which it crystallises in soft, white needles melting at 127—128°; it is decomposed by caustic soda.

By the action of nitrous acid on cyanethine in glacial acetic solution, the hydroxy-base is obtained (Abstr., 1883, 352); but by heating the solution and using an excess of nitrous acid, this is further acted on, and a yellow oil, which solidifies on cooling, is obtained when the liquid is poured into hot water. This is dissolved in weak aqueous soda, and the solution dropped into dilute hydrochloric acid. White flocks of the substance $C_9H_{12}N_4O_5$ separate, and when dried are crystallised from benzene as beautiful, lustrous laminæ melting at 136°, soluble in alcohol, ether, chloroform, and ammonia (unchanged), and in 5320 parts of water at 24°. The yield is 60 per cent. of the cyanethine taken. This substance is a derivative of hydroxymethyldiethylmetadiazine, but not a dinitro-derivative. By reducing it with sodium amalgam in weak alkaline solution, *isonitrosohydroxymethyldiethylmetadiazine*, $NOH{:}C_9N_2H_{11}{\cdot}OH$, is obtained; it is precipitated by neutralising with hydrochloric acid, and crystallises from weak alcohol in aggregates of beautiful, lustrous, soft needles melting at 205°, soluble in alcohol, in ether, and in 2490 parts of water at 17°. It is a feeble acid, and forms an insoluble *copper* salt. Its *silver* salt, $C_9H_{12}AgN_3O_2$, is described. It is converted into hydroxymethyldiethylmetadiazine by hydriodic acid, and into the substance $C_9H_{12}N_4O_5$ by nitrous acid.

The *phenylhydrazone* compound, $N_2HPh{:}C_9N_2H_{11}{\cdot}OH$, is formed when the substance $C_9H_{12}N_4O_5$ in acid alcoholic solution is heated with phenylhydrazine hydrochloride at 150°; it crystallises in thin, yellow prisms melting above 275°. It is also formed by treating the above isonitroso-compound in the same way.

Concentrated hydrochloric acid at 160° decomposes the substance

$C_9H_{12}N_4O_5$ with formation of carbonic anhydride, ammonia, and a *hydroxydiethylmetadiazinecarboxylic acid*,



$$\mathrm{CEt}<\begin{matrix}\mathrm{N{=\!=}CEt}\\ \mathrm{N\cdot C(OH)}\end{matrix}>\mathrm{C\cdot COOH},$$

which crystallises in aggregates of prisms, melting with decomposition about 244°. Its *silver* salt has been obtained. A. G. B.

Constitution of Allyl Cyanide. By C. PALMER (*Amer. Chem. J.*, **11**, 89—93).—Bromine (11·8 grams) dissolved in dry carbon bisulphide (5 vols.) was allowed to drop into a solution of allyl cyanide (b. p. 116°, 5 grams) in dry carbon bisulphide (equal vols.) kept in ice. When colourless, the carbon bisulphide was distilled off in a vacuum without the aid of heat. By distilling the residue at 13 mm. pressure, *dibromobutyl cyanide* was obtained as a heavy oil of a pungent odour, attacking the eyes and nose; it boils with partial decomposition below 110° (13 mm. pressure). The dibromobutyl cyanide (12 grams) was dissolved in 90 per cent. alcohol (20 c.c.) and saturated with hydrogen chloride at 5°; there were thus obtained *ethyl αβ-dibromobutyrate*, an oil boiling in a vacuum at 104—105°, and *αβ-dibromobutyramide*, $CHMeBr\cdot CHBr\cdot CONH_2$, which crystallises in flat plates, freely soluble in ether and alcohol, sparingly so in water, and melting at 150—151°; it yields αβ-dibromobutyric acid when heated with hydrochloric acid.

As nothing besides ethyl αβ-dibromobutyrate and αβ-dibromobutyramide can be obtained from the bromocyanide formed by the action of bromine on allyl cyanide, the constitution of the latter is $CH_3\cdot CH{:}CH\cdot CN$. A. G. B.

Succinamonitrile. By R. DROUIN (*Compt. rend.*, **108**, 675—677).—The action of alcoholic ammonia on ethylene cyanide in sealed tubes at 110° for several hours yields a readily crystallisable substance of the composition $C_4H_6N_2O$, which forms colourless, monoclinic crystals, only slightly soluble in alcohol, and insoluble in ether, chloroform, terebenthene, light petroleum, and carbon bisulphide. It decomposes slowly in cold water and rapidly in hot water, with evolution of ammonia. When heated at 210—220°, it decomposes without melting, and yields a brown residue, ammonia, and a sublimate which forms small needles. If boiled with potassium hydroxide, it yields succinic acid, and hence is the nitrile of succinamic acid, and has the constitution $CN\cdot C_2H_4\cdot CONH_2$. It is the first example of a compound with the function of both a nitrile and an amide.

If the alcohol used in the preparation contains too much water, the products are succinic diamide, succinamic acid, or even succinic acid if the proportion of water is large. There can be little doubt that the water which combines with the molecule of ethylene is derived from the alcohol, and that ethylamine is formed at the same time, but the latter could not be separated from the large quantity of ammonia with which it is mixed. C. H. B.

Preparation of Alkyl Chlorides from Alcohols. By H. MALBOT (*Compt. rend.*, **108**, 747—749).—The method of preparing alkyl chlorides by saturating alcohols with gaseous hydrogen chloride and heating the liquids in closed vessels, does not yield satisfactory results, because the excess of hydrochloric acid present is too small to prevent saponification by the water. If, however, the alcohol is saturated with hydrogen chloride, and then mixed with a quantity of the strongest aqueous solution of the acid, etherification takes place rapidly, and becomes almost complete even at a moderate temperature. The proportion of water present of course increases as the reaction proceeds, but hydrochloric acid is always present in sufficient excess to prevent saponification. C. H. B.

Seminose. By R. REISS (*Ber.*, **22**, 609—613).—In view of the fact that microscopical methods afford but little information as to the nature of the cellulose stored up as reserve food material in seeds, the author has studied the action of hydrolytic agents on the cellulose forming the thick-walled cells of the endosperm of vegetable ivory nuts. When thin shavings of this material are digested with dilute sulphuric acid, a sugar, *seminose*, is obtained, which forms a thick, non-crystallisable syrup. It has a sweet taste, and a pleasantly bitter after-taste, is dextrorotatory, reduces Fehling's solution, and is fermentable by yeast. The *hydrazone*, $C_{12}H_{18}N_2O_5$, crystallises in small, colourless, rhombic tables, and melts at 185—186°. On treatment in neutral aqueous solution with lead acetate, seminose forms a white, gelatinous lead compound, $C_6H_{12}O_6,PbO + H_2O$, which is sparingly soluble in hot and cold water. Like galactose (Rischbieth, Abstr., 1888, 40), seminose yields an *isonitroso*-compound, $C_6H_{13}O_6N$, crystallising in colourless forms melting at 176°.

W. P. W.

Mannose. By E. FISCHER and J. HIRSCHBERGER (*Ber.*, **22**, 1155—1156; compare preceding Abstract).—Mannose forms a lead salt which is sparingly soluble in cold water. The *oxime*, $C_6H_{13}O_6N$, is crystalline, and is very soluble in hot water, but practically insoluble in absolute alcohol. When rapidly heated, it melts at about 184° with decomposition, but when heated more slowly, it melts at 176—180°. The hydrazone has already been found by the authors to melt at about 188° with decomposition when heated slowly (Abstr., 1887, 567; 1888, 934), hence there can be no doubt that Reiss' seminose is identical with mannose. W. P. W.

Sugar-like Compound from Laminaria. By R. W. BAUER (*Ber.*, **22**, 618).—When *Laminaria*, after extraction with alcohol, is treated with dilute sulphuric acid (1 to 30) at 100° for 12 hours, and the filtrate neutralised with chalk, evaporated to a syrup, and again extracted with alcohol, a filtrate is obtained which after slow evaporation in a desiccator over sulphuric acid yields a crystalline mass having a distinctly sweet taste. Its specific rotatory power $[\alpha]_D = 46{\cdot}71°$ at 14°, and with phenylhydrazine it forms a crystalline compound melting at about 140°. W. P. W.

Amines of the Methyl and Ethyl Series. By A. W. HOFMANN (*Ber.*, **22**, 699—705).—Methylamine, prepared by recrystallising the hydrochloride several times, boils at —6° to —5·5° under 768·35 mm. pressure. Sp. gr. = 0·699 at —10·8°. The liquid base fumes strongly in air. It could not be obtained in the solid state at —75° and 10 mm. pressure.

Dimethylamine was prepared by the action of methyl bromide on ammonia, converting the base into the nitroso-derivatives, and separating with hydrochloric acid and distilling several times over sodium. It boils at 7·2° to 7·3° under 764·1 mm. pressure (compare *Proc. Roy. Soc.*, **12**, 382). Sp. gr. = 0·6865 at —5·8°. It could not be got to solidify.

Trimethylamine was prepared from tetramethylammonium hydroxide and distilled over sodium. It boils at 3·2° to 3·8° under 764·6 mm. pressure. Sp. gr. = 0·662 at —5·2° (compare Winkles, this Journal, 7, 62, and Hofmann, *loc. cit.*). The base remains liquid at —75° under 10 mm. pressure. It yields a crystalline hydrate (with 7 mols. H_2O) melting at 4·3°.

Ethylamine has the boiling point ascribed to it by Wurtz (*Ann. Chim. Phys.* [3], **30**, 471). Sp. gr. 0·708 at —2°.

Diethylamine boils at 55·5° to 56° under 767·8 mm. pressure. Sp. gr. = 0·7107 at 15° (compare Hofmann, *Proc. Roy. Soc.*, **11**, 67, and Oudemans, *Rec. Trav. Chim.*, **1**, 59). It crystallises readily at —50° under the ordinary pressure, and melts at —40°.

Triethylamine boils at 89—90° under 767·8 mm. pressure. Sp. gr. = 0·735 at 15°. Both mono- and tri-ethylamine remain liquid at —75° under 10 mm. pressure.

The apparatus used for determining the boiling points, which was similar to that used by Bannow (*Chem. Ind.*, 1886, 328), is described.

N. H. M.

Conversion of Palmitonitrile into Hexadecylamine. By F. KRAFFT and A. MOYE (*Ber.*, **22**, 811—815).—*Hexadecylamine*, $C_{16}H_{33}\cdot NH_2$, can be obtained by heating ethyl iodide with alcoholic ammonia, but it is most easily prepared by gradually adding sodium (4 parts) to an alcoholic (30 parts) solution of palmitonitrile (3 parts) first at the ordinary temperature, and then after two to three hours heating very gradually to 120° until the sodium is completely dissolved. The whole is poured into a large quantity of water, the solution acidified with hydrochloric acid, the precipitate dissolved in a small volume of alcohol, and reprecipitated with ether. The *hydrochloride*, $C_{16}H_{33}\cdot NH_2,HCl$, is thus obtained in shining plates, and the yield is 75 per cent. of the palmitonitrile employed. The *platinochloride* has the composition

$$(C_{16}H_{33}\cdot NH_2)_2,H_2PtCl_6.$$

The *hydriodide* crystallises in small plates, melts at about 170—172° with decomposition, and is sparingly soluble in cold alcohol. The *base*, prepared by distilling the hydrochloride first with soda and then with sodium in a partial vacuum, melts at 45—46°, boils at 330° (at 187°, 15 mm.), and is almost insoluble in water. On exposure to the air, it rapidly absorbs carbonic-anhydride.

Ethylhexadecylammonium iodide, $C_{16}H_{33}\cdot NH_2EtI$, separates in crystalline plates, melting at 162—166° with decomposition when hexadecylamine is heated at about 150° for 3—4 hours with excess of ethyl iodide. *Ethylhexadecylamine*, $NHEt\cdot C_{16}H_{33}$, prepared by warming the ammonium iodide with concentrated potash and distilling the product over sodium in a partial vacuum, is a colourless, crystalline compound melting at 27—28°, and boiling at 342° (corr.) with partial decomposition (b. p. 195—196°, 15 mm.).

Diethylhexadecylamine, $NEt_2\cdot C_{16}H_{33}$, is formed, together with the ammonium iodide, when ethyl iodide (5 parts) is heated with diethylamine (2 parts) at 150°; the crude product is warmed with potash and distilled over sodium. It is a crystalline compound melting at 6—8°, and boiling at 355° (corr.) (204—206°, 15 mm.). The *platinochloride* has the composition $(NEt_2\cdot C_{16}H_{33})_2,H_2PtCl_6$.

Triethylhexadecylammonium iodide, $NEt_3C_{16}H_{33}I$, melts at about 180—181° with decomposition. F. S. K.

Combination of Chloral with Glycol. By DE FORCRAND (*Compt. rend.*, **108**, 618—620).—147·5 grams of anhydrous chloral were mixed with 62 grams of glycol. There is a notable development of heat, and the product is a homogeneous, viscid liquid, which after remaining in a well-closed vessel for several weeks gradually solidifies to a mass of hard, transparent crystals of the composition $C_2HCl_3O,C_2H_4(OH)_2$. This compound is soluble in water, melts at 42°, and its heat of formation from the constituent liquids is +15·4 Cal.

When chloral is mixed with glycerol, there is development of heat, but the product will not crystallise. The heat of combination of chloral with glycol is greater than its heat of combination with ethyl alcohol. It follows that Henry's law, that the heat of combination of chloral with alcohols diminishes as the molecular weight of the alcohol increases, is not general, although it may hold good for alcohols of the same series. C. H. B.

Preparation of Oximes. By K. AUWERS (*Ber.*, **22**, 604—606).—The author finds that the preparation of oximes is much facilitated by allowing the reaction between hydroxylamine and the ketone to take place in alkaline solution. The best results are obtained by employing 3 mols. of sodium hydroxide with 1 mol. of hydroxylamine hydrochloride; not only is the oxime prepared in a much shorter time than by using equimolecular proportions of these substances, but the yield also is, in many cases, almost that theoretically possible. The excess of alkali, however, cannot, of course, be employed in those cases in which either a dioxime is formed which readily undergoes conversion into its anhydride in the presence of alkali, or in which the ketone is attacked by the alkali. W. P. W.

Solid Acetone-chloroform and its Derivatives. By C. WILLGERODT and F. DÜRR (*J. pr. Chem.* [2], **39**, 283—289; compare Abstr., 1887, 570 and 1030).—*Tertiary bromobutyric tribromide* is obtained by the action of phosphorus pentabromide on acetone-chloroform; it is a colourless solid, subliming at 160° without melting, and boiling between 185° and 190°.

Tertiary acetoxybutyric trichloride, $COMe·O·CMe_2·CCl_3$, is formed from acetone-chloroform and either acetic chloride or anhydride; it boils at 191°.

Tertiary benzoxybutyric trichloride, $COPh·O·CMe_2·CCl_3$, prepared from benzoic chloride and acetone-chloroform, is a yellow oil boiling at 282°.

Acetone-chloroform is very little reduced by sodium amalgam. With zinc and hydrochloric acid, a considerable quantity of trimethyl carbinol is obtained. With zinc and glacial acetic acid, pseudobutyl acetate is formed, whilst hydriodic acid reduces it to a hydrocarbon, probably isobutane.

The authors have not succeeded in displacing the chlorine in acetone-chloroform by alkyl radicles. A. G. B.

Dihydroxystearic Acid. By M. GRÖGER (*Ber.*, **22**, 620—622).—A comparison of the properties of the acid supposed to have the composition $C_{26}H_{52}O_6$, obtained by oxidising the fatty acids of tallow with potassium permanganate in alkaline solution (Abstr., 1885, 883) with those of Saytzeff's dihydroxystearic acid (Abstr., 1886, 140), shows that the two substances are identical. The melting point was, however, found to be 125—125·5° by Piccard's method, and 130·5—131·5° when taken in a capillary tube without previous fusion, whilst the fused acid melted in a capillary tube at 126·5—128·5°; the solidifying point was 120—121°. W. P. W.

Boiling Points in the Oxalic and Oleic Acid Series. By F. KRAFFT and H. NOERDLINGER (*Ber.*, **22**, 816—820).—When malonic acid is heated almost to its melting point under a pressure of 8—10 mm., it sublimes unchanged, but when more strongly heated it is decomposed into acetic acid and carbonic anhydride.

Succinic acid sublimes unchanged when heated under the same pressure at a temperature below its melting point, but when heated more strongly it is converted into the anhydride. If the retort is provided with two receivers, one of which is kept warm to prevent the water condensing, the anhydride is obtained almost pure, and can be obtained quite anhydrous by redistilling. Succinic acid has the following boiling points:—131°, 10 mm.; 139°, 15 mm.; 169°, 50 mm.; 189°, 100 mm.; 261° under the ordinary pressure.

Trimethylene cyanide has the following boiling points, the thermometer being entirely placed in the vapour:—142°, 10 mm.; 149°, 15 mm.; 181·1°, 50 mm.; 203°, 100 mm.

When glutaric acid, in small quantities, is heated quickly to its boiling point under a pressure of 10 mm., it distils almost entirely between 195° and 198°, and only slight decomposition occurs. When heated under the same pressure with a reflux condenser for 2—3 hours, it gradually loses water, and is completely converted into the anhydride. Glutaric anhydride boils, under the ordinary pressure, at 286—288° (corr.) with only very slight decomposition; under 10 mm.

pressure, it boils at 150°, under 15 mm. at 158°, under 50 mm. at 189°, and under 100 mm. at 211°.

The following table gives the boiling points under various pressures of several acids of the oxalic acid series:—

Pressure in mm. mercury.	Adipic acid, $C_6H_{10}O_4$, m. p. 149—149·5°.	Pimelic acid, $C_7H_{12}O_4$, m. p. 103°.	Suberic acid, $C_8H_{14}O_4$, m. p. 140°.	Azelaic acid, $C_9H_{16}O_4$, m. p. 106°.	Sebacic acid, $C_{10}H_{18}O_4$, m. p. 133—133·5°.
10	205·5°	212°	219·5°	225·5°	232°
15	216·5	223	230	237	243·5
50	244·5	251·5	258·5	265	273
100	265	272	279	286·5	294·5

All the acids in the above table distil without the slightest decomposition under the pressures given, except that of 100 mm., under which pressure very slight decomposition occurs; under the ordinary pressure, the boiling point is about 70° higher than under 100 mm.

The following table gives the boiling points of several acids of the oleic acid series, acids which are readily decomposed when heated under the ordinary pressure:—

Pressure in mm. mercury.	Oleic acid, $C_{18}H_{34}O_2$.	Elaidic acid, $C_{18}H_{34}O_2$.	Erucic acid, $C_{22}H_{42}O_2$.	Brassidic acid, $C_{22}H_{42}O_2$.
10	223°	225°	254·5°	256°
15	232·5	234	264	265
30	249·5	251·5	281	282
50	264	266	—	—
100	285·5—286°	287·5—288°	—	—

Elaidic acid and stearic acid boil at almost exactly the same temperature under the same conditions. F. S. K.

Calcium and Strontium Malonates. By MASSOL (*Compt. rend.*, **198**, 813—816).—Attempts to obtain calcium hydrogen malonate in a crystalline form were unsuccessful. The normal salt crystallises with 4 mols. H_2O below 15°, and forms brilliant, silky needles, only slightly soluble in water. When it crystallises above 35° it forms small, brilliant scales, which contain 2 mols. H_2O, and are only very slightly soluble in water. The anhydrous salt is obtained by heating either of the hydrates at 135° for many hours in a current of hydrogen. Since the hydrated and anhydrous salts are so sparingly soluble in water, the determinations of the heats of solution, &c., were made by dissolving them in a solution of malonic acid.

$C_3H_4O_4$ solid + $Ca(OH)_2$ solid = $C_3H_2O_4Ca$ solid + $2H_2O$ solid .... develops +20·75 Cal.
C_3 solid + H_2 gas + Ca solid + O_4 gas = $Ca_3H_2CaO_4$ solid .... „ +311·89 „
$Ca_3H_2O_4Ca$ solid + $2H_2O$ solid = $C_3H_2O_4Ca,2H_2O$ solid .... „ +4·74 „
$Ca_3H_2O_4Ca$ solid + $4H_2O$ solid = $C_3H_2O_4Ca,4H_2O$ solid .... „ +10·146 „

The heat of formation of calcium malonate is practically the same as that of the oxalate, and is lower than the heat of formation of the acetate. This is also true in the case of the strontium salt.

$C_3H_4O_4$ sol. + $Sr(OH)_2$ sol. = $C_3H_2O_4Sr$ solid + $2H_2O$ solid .... develops +32·30 Cal.
C_3 solid + H_2 gas + Sr solid + O_4 gas = $C_3H_2O_4Sr$ solid .... „ +325·04 „

C. H. B.

The Symmetrical Dimethylsuccinic Acids. By N. ZELINSKY and S. KRAPIVIN (*Ber.*, **22**, 646—654).—The *methyl* salt of the "maleïnoid" symmetrical dimethylsuccinic acid (m. p. = 123°), prepared by heating the silver salt with methyl iodide at 100° for 6—8 hours, boils at 199—200°, and is a colourless, mobile liquid with a pleasant odour. On saponification with alcoholic potash, it yields the "maleïnoid" acid exclusively. The *ethyl* salt, prepared in like manner, is a colourless liquid, and boils at 221—222° under a pressure of 761 mm. Its sp. gr. is 1·0218 at 0° and 1·0072 at 16° (compared with water at 0°). When heated at 310° in a Victor Meyer apparatus, its vapour-density is 4·01, which indicates almost complete dissociation into ethylic ether and dimethylsuccinic anhydride; the vapour-density is, however, normal ($d = 6·817$) when determined in a Hofmann apparatus heated at 184°. On saponification the ethyl salt seems to yield the "maleïnoid" acid exclusively. When, however, the ethyl salt is prepared by saturating the cooled alcoholic solution of "maleïnoid" dimethylsuccinic acid with hydrogen chloride, it boils at 219—220° under a pressure of 745 mm., and on saponification yields a mixture of the "maleïnoid" and "fumaroid" (m. p. = 192°) dimethylsuccinic acids. The *barium* salt, with 3 mols. H_2O, and *calcium* salt, with 2 mols. H_2O, are described. The *imide*, prepared by distilling the dry ammonium salt of the "maleïnoid" acid in a current of ammonia, crystallises from alcohol in stellate groups of prisms, and melts at 109—110°.

The *methyl* salt of the "fumaroid" symmetrical dimethylsuccinic acid, prepared by the action of methyl iodide on the silver salt, boils at 198—199°, and on saponification yields the "fumaroid" acid exclusively. The *ethyl* salt, prepared in like manner, boils at 219·5°, has a sp. gr. of 1·0130 at 0°, and 1·0022 at 12° (compared with water at 0°), and on saponification yields the "fumaroid" acid. Its vapour-density as determined by V. Meyer's method at 310° is 3·78, and by Hofmann's method at 185° is 6·92. When obtained by treating the alcoholic solution of "fumaroid" dimethylsuccinic acid with hydrogen chloride, the ethyl salt boils at 220° under a pressure of 757 mm., and on saponification yields a mixture of the "maleïnoid" and "fumaroid" acids. The *barium* salt, with 4 mols. H_2O, and *calcium* salt, with 1 mol. H_2O, are described. The *imide* crystallises in aggregates which resemble those of the imide of the "maleïnoid" acid, and melt like these at 109—110°. On bromination, the "fumaroid" acid is converted into pyrocinchonic anhydride. W. P. W.

Reduction of Tartaric Acid. By M. Ballo (*Ber.*, 22, 750—754; compare Abstr., 1884, 765).—Neither Liebig's nor Baeyer's theory of the formation of sugar in plants gives any explanation of the part played by the iron which is present in chlorophyll. In investigating the action of this metal on vegetable acids, the author found that tartaric acid, when warmed with ferrous sulphate, is converted into an acid which he names isoarabinic acid, on account of the sticky nature of solutions of the calcium salt. Tartaric acid (1 part) and ferrous sulphate (1 part) are dissolved in water (about 2 parts) and the solution warmed on the water-bath; after a short time a greenish-yellow precipitate, consisting chiefly of the iron salt of an acid containing more oxygen than isoarabinic acid, is formed. The whole is then evaporated with constant stirring, until the residue solidifies on cooling, and is then extracted with strong alcohol. The alcohol is evaporated, the residue dissolved in water, the solution neutralised with milk of lime, filtered, evaporated to a syrup, and the calcium salt which separates dissolved in water and decomposed with the calculated quantity of oxalic acid. The filtered solution is concentrated, mixed with alcohol, separated from any undecomposed salt, and again concentrated and mixed with alcohol and ether. After keeping for a long time, a crystalline compound, which the author names isoarabinic acid hydrate separates, and the filtered solution, on evaporation, yields isoarabinic acid.

Isoarabinic acid, $C_6H_{10}O_6$, is a thick, almost colourless syrup, which is miscible with water in all proportions, and when burnt gives off a smell of burnt sugar. It is dextrorotatory, and its specific rotatory power is $[\alpha]_D = +20°$, but it does not reduce Fehling's solution. The *potassium* salt, $C_6H_9O_6K$, is anhydrous, and crystallises well. The *calcium* salt, $(C_6H_9O_6)_2Ca + 9H_2O$, dissolves in water, forming a sticky solution, from which it crystallises moderately easily; it loses some of its water at 100—120°, the remainder only at a temperature so high (above 140°) that the salt is partially decomposed. It reduces ammoniacal silver solution, and readily decomposes both in solution and in the dry state, being converted into a basic salt, $(C_6H_9O_6)_2Ca,CaO + 8H_2O$. The latter is a colourless powder, and is insoluble in water, but it dissolves in potash, and is reprecipitated on boiling the solution; it reduces ammoniacal silver solution. When a solution of the calcium salt is mixed with a solution of lead acetate, a yellowish precipitate, consisting principally of the salt, $(C_6H_9O_6)_2Pb$, is formed, and a colourless substance, consisting principally of the basic salt, $(C_6H_9O_6)_2Pb,2PbO$, separates from the filtrate after some time.

Isoarabinic acid hydrate (see above) has probably the composition $C_6H_{12}O_6$; it does not reduce Fehling's solution.

These results show that substances, isomeric with the carbohydrates, and other compounds richer in oxygen, are formed by the action of ferrous sulphate on tartaric acid. The quantity of ferrous sulphate employed may be as little as one-tenth the weight of the tartaric acid without influencing the results, but the author believes that direct sunlight may have some appreciable effect on the reaction. These facts are evidence in favour of Liebig's theory of the formation of sugar in plants. It was frequently observed that the crude solutions of isoarabinic acid contain reducing substances which, however, disappeared on further investigation; this fact seems to indicate that it is possible to obtain sugar synthetically from tartaric acid or other vegetable acids. F. S. K.

Action of Methyl Diazoacetate on Ethereal Salts of Unsaturated Acids. By E. BUCHNER (*Ber.*, **22**, 842—847; compare Abstr., 1888, 1274).—*Methyl acetylenedicarboxylodiazoacetate*, $C_3HN_2(COOMe)_3$, is prepared by mixing methyl acetylenedicarboxylate (1 mol.) with methyl diazoacetate (1 mol.), and immediately adding an equal volume of ether, otherwise a very violent reaction occurs with evolution of light and heat, 1 gram of the mixture giving out 199·4 gram-cal. as a mean of two experiments. As soon as the mixture begins to get warm, the vessel is cooled and, when the reaction is at an end, which is generally the case in about an hour, the ether can be directly evaporated, and the residue recrystallised from methyl alcohol, from which it separates in compact crystals. It crystallises from hot water in needles, melts at 118°, and is very readily soluble in methyl alcohol, but only moderately so in ether. It is not acted on by warm, concentrated sulphuric acid, but it dissolves in soda with a transient yellow coloration. The molecular weight, determined by Raoult's method, was found to be 254 as the average of six experiments. When heated at 220°, it is partially decomposed with evolution of carbonic anhydride; if the residue is heated in a partial vacuum, the anhydride distils at 202° (30 mm.), and soon solidifies. This *anhydride*, $COOMe\cdot C_3HN_2<\genfrac{}{}{0pt}{}{CO}{CO}>O$, crystallises from ether, melts at 70°, and is readily soluble in water.

Acetylenedicarboxylodiazoacetic acid, $C_6H_4N_2O_6$, prepared by boiling the ethereal salt with dilute sulphuric acid, crystallises in small needles, melts at 233° with evolution of carbonic anhydride, and is more sparingly soluble in cold than in hot water. It is not acted on by cold, alkaline potassium permanganate. The *sodium hydrogen* salt, $C_6H_3N_2O_6Na$, prepared by treating the acid with the calculated quantity of soda, crystallises from hot water in long needles, and is sparingly soluble in cold water. The *silver* salt is very sparingly soluble in water, and when heated, it explodes slightly, yielding an oil which is probably identical with the compound described below.

When the tricarboxylic acid is heated at 230—240° it melts, with evolution of large quantities of carbonic anhydride, but gradually solidifies again, and on continued heating distils in the form of a colourless oil, leaving a slight residue of some solid, colourless substance. The oil solidifies on cooling, and crystallises from light petroleum in colourless needles melting at 69°. It has a slight pyridine-like odour, and is very readily soluble in water, alcohol, ether, and benzene. Its molecular formula is either $C_3H_4N_2$ or $C_6H_8N_4$, but molecular weight determinations by Raoult's method gave 79, 95, and 102 with benzene solutions containing 0·148, 0·351, and 0·495 per cent. respectively. It volatilises perceptibly in a partial vacuum; aqueous solutions have a slight acid reaction, and give a white, stable salt with silver nitrate. It is not acted on by cold potassium permanganate, and it does not give Knorr's pyrazole reaction. F. S. K.

Base containing Chromium and Carbamide. By W. J. SELL (*Proc. Roy. Soc.*, **45**, 321—345; compare Abstr., 1883, 178).—The author has examined the green, crystalline substance obtained by the action of chromyl dichloride on carbamide, and subsequent treatment with water. Its composition is difficult to determine, since it is decomposed by water, and is insoluble in most other menstrua. It can, however, be recrystallised from dilute hydrochloric acid. The reactions and analytical data favour the formula $Cr_2(CON_2H_4)_{12}Cl_2(Cr_2O_7)_2,2H_2O$. Crystallographic measurements are given. The substance dissolves in strong hydrochloric acid, giving dichlorotetrachlorochromate of the base $Cr_2(CON_2H_4)_{12}Cl_2,4CrO_3Cl,3H_2O$, which is decomposed by water, reproducing the original salt, hence it is probable the latter salt is the first product of the action of chromyl dichloride on carbamide, and that the dichloro-compound is due to the action of water. The product of the action of chromyl dichloride and carbamide alone cannot be purified. A number of salts of the base are described. H. K. T.

Aluminium Methide. By F. QUINCKE (*Zeit. physikal. Chem.*, **3**, 164—169).—The author has determined the vapour-density of aluminium methide by the displacement method at a temperature of 10° above its boiling point. As the mean of a number of experiments he gets the number 3·924, and as this is 20 per cent. smaller than that corresponding with the formula Al_2Me_6, given by Louïse and Roux (Abstr., 1888, 583), he concludes that the molecule of aluminium methide can only be expressed by $AlMe_3$. H. C.

Methylfurfuraldehyde and the Corresponding Methylpyromucic Acid. By H. B. HILL (*Ber.*, **22**, 607—608).—After repeated fractionation, the oil containing furfuraldehyde which is obtained by the dry distillation of wood (this Journal, 1877, ii, 746), yields a fraction boiling at 184—186°; this exhibits all the properties of an aldehyde, and most probably consists of methylfurfuraldehyde. When purified by means of the sodium hydrogen sulphite compound, it boils at 186·5—187° (thermometer in vapour) under a pressure of 756 mm. It dissolves in about 30 parts of cold water, and its aqueous solution on treatment with ammonia forms a well-crystallised compound, $N_2(C_6H_6O)_3$, melting at 86—87°. When oxidised, it yields a methylpyromucic acid, $C_6H_6O_3$, which closely resembles pyromucic acid, but melts at 108—109°, and dissolves somewhat more readily in water, benzene, and chloroform; its *silver* salt, $C_6H_5O_3Ag$, crystallises in slender needles, and is very sparingly soluble in hot water.

W. P. W.

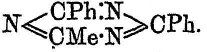
Tetrabromodinitrobenzene. By C. L. JACKSON and W. D. BANCROFT (*Ber.*, **22**, 603—604; compare Abstr., 1888, 1276).—Tetrabromodinitrobenzene reacts with a number of substances; few of the products have, however, been investigated. The compound obtained by heating it with aniline on a water-bath has the composition $C_6Br(NHPh)_3(NO_2)_2$, and crystallises in microscopic, red prisms melting at 175—176°.

W. P. W.

Preparation of Metanitrotoluene. By K. BUCHKA (*Ber.*, **22**, 829—833).—Metanitrotoluene (compare Beilstein and Kuhlberg, *Annalen*, **155**, 24) is best prepared as follows:—Pure metanitroparatoluidine, prepared by Gattermann's method (*Ber.*, **18**, 1482), is dissolved in alcohol (3 parts) and concentrated sulphuric acid (about 3 parts), and a saturated aqueous solution, containing rather more than the calculated quantity of sodium nitrite, is added drop by drop to the cold solution. As soon as all the sodium nitrite is added, the solution is kept for some time, then carefully warmed until the evolution of nitrogen has ceased, and the liquid has assumed a dark-brown colour. The alcohol is evaporated, the product distilled with steam as long as oil passes over, and the metanitrotoluene extracted with ether. The product thus obtained distils entirely between 228° and 231°, and solidifies when cooled, melting again at 16°. The yield is from 66—84 per cent. of the theoretical quantity, but in one experiment as much as 90 per cent. was obtained. The residue contains a brown, resinous, non-volatile substance, from which no crystalline compound could be isolated.

F. S. K.

Tricyanides. By F. KRAFFT and A. v. HANSEN (*Ber.*, **22**, 803—811).—*Methyldiphenyl tricyanide*, $C_{16}H_{13}N_3$, is obtained, together with benzoic acid, by adding aluminium chloride (2 parts) to a mixture of benzonitrile (5 parts) and acetic chloride (2 parts) cooled to 0°, and raising the temperature to 70° in the course of 18 hours. The whole is then poured into ice-cold water, the product extracted with ether, and fractionated in a partial vacuum. It crystallises from alcohol in slender needles, melts at 110°, boils at 227° (15 mm.), is soluble in light petroleum, and has feeble basic properties. The *hydrochloride* separates in small needles when hydrogen chloride is passed into a benzene solution of the base, but the salt is decomposed by cold water, or when heated at 150°, yielding the pure base. The *platinochloride*, $(C_{16}H_{13}N_3)_2,H_2PtCl_6$, prepared by precipitating a warm alcoholic solution of the hydrochloride with platinum chloride, separates in small, yellowish-red crystals, and is decomposed by water. When the base is boiled for a long time with potash, small quantities of ammonia are evolved, and traces of benzoic acid are obtained, but when heated for a few hours with dilute (1 : 3) sulphuric acid, it is entirely decomposed into benzoic acid, acetic acid, and ammonia.

The vapour-density, determined at 444°, was found to be 122, and the constitution of this compound is probably  $N\langle{}^{CPh:N}_{CMe\cdot N}\rangle CPh$.

Ethyldiphenyl tricyanide, $C_{17}H_{15}N_3$, prepared in like manner from propionic chloride, is a crystalline compound melting at 67°, and boiling at 233—234° (15 mm.). The *hydrochloride* and the *platinochloride*, $(C_{17}H_{15}N_3),H_2PtCl_6$, are decomposed by water. The vapour-density, determined by V. Meyer's method, was found to be 129°, and its constitution is probably analogous to that of the preceding compound.

Propyldiphenyl tricyanide, $C_{18}H_{17}N_3$, crystallises from alcohol, melts at 78·5°, and boils at 239° (15 mm.); its vapour-density was found to be 140. When boiled with moderately dilute sulphuric acid, it is quickly decomposed into ammonia, butyric acid, and benzoic acid. The *platinochloride*, $(C_{18}H_{17}N_3)_2,H_2PtCl_6$, crystallises in small, yellowish-red needles, and is decomposed by water.

Hexyldiphenyl tricyanide, $C_{21}H_{33}N_3$, melts at 44°, and boils at 265° (15 mm.). The *platinochloride* has the composition

$$(C_{21}H_{33}N_3)_2,H_2PtCl_6.$$

Pentadecyldiphenyl tricyanide, $C_{30}H_{41}N_3$, is prepared by adding aluminium chloride (3 parts) to a mixture of benzonitrile (5 parts) and palmitic chloride (3 parts), and gradually heating the mixture to 100° in the course of 60 hours. It separates from isobutyl alcohol in plates, melts at 64°, boils at 327—328° (13 mm.), and is readily soluble in ether and hot alcohol, but only sparingly in cold alcohol. It is not decomposed when heated at 120—125° with alcoholic potash or when melted with potash, but when heated with moderately dilute sulphuric acid it is slowly decomposed, yielding benzoic acid and ammonia.

F. S. K.

Iodation of Phenols in Ammoniacal Solution. By C. WILLGERODT and A. KORNBLUM (*J. pr. Chem.* [2], **39**, 289—298; compare Abstr., 1888, 940).—*Iodothymol* is prepared by adding powdered iodine (8·5 grams) by degrees to a solution of thymol (5 grams) in ammonia (6 c.c.) mixed with alcohol (2 c.c.); the oil which is formed is distilled with steam. When pure, iodothymol crystallises in lustrous, white needles melting at 69° and soluble in all solvents except water. It is oxidised to thymoquinone by manganese dioxide and sulphuric acid or by ferric chloride. Phosphoric anhydride liberates iodine from it in the cold, but does not convert it into iodocresol. It is not decomposed by aqueous potash at 160—300°, and even if melted with potassium hydroxide at 130° it is not converted into hydrothymoquinone. Moist silver oxide does not remove the iodine.

Iodocymyl ethyl ether, obtained from potassium iodothymol and ethyl iodide, crystallises in opaque, white, rhombic tables melting at 52°, insoluble in cold water, slightly soluble in hot water and alcohol, freely in other solvents. *Iodocymyl acetate* forms white needles melting at 71°, and soluble in the usual solvents. *Iodocymyl benzoate* crystallises in large tables melting at 95°; the crystallographical measurements are given. *Iodocymyl picrate* forms yellowish aggregates of crystals melting at 155°.

Diiodorthocresol is prepared from orthocresol and iodine as directed for iodothymol. It crystallises in needles melting at 69·5°, and is soluble in all organic solvents. *Diiodorthocresyl acetate* crystallises in white tables melting at 56°, and soluble in all organic solvents. *Diiodorthocresyl picrate* forms bright yellow aggregates of crystals melting at 204°.

The iodoparacresols have been described by Schall and Dralle (Abstr., 1885, 146). *Diiodoparacresyl ethyl ether* is a white solid melting at 77°, and soluble in the usual organic solvents.

Iodometacresol was obtained as an oil, and *diiodometacresol* as long needles melting at 76°, and soluble in the usual solvents.

A. G. B.

Metamidoparacresyl Methyl Ether. By C. Schall (*Ber.*, **22**, 749).—Homomethylsalicylic acid (methoxytoluic acid),

$$[COOH : OMe : Me = 1 : 2 : 5],$$

according to Limpach (this vol., p. 499), melts at 70°; the melting point (67°) previously given by the author is too low, probably owing to the presence of a trace of water.

Chloroparacresol methyl ether boils at 213—215° (corr.) (compare Limpach, *loc. cit.*), and was first prepared by Schall and Dralle.

F. S. K.

Amidoparacresyl Methyl Ether. By L. Limpach (*Ber.*, **22**, 789—791).—*Nitracetamidoparacresyl methyl ether*,

$$[Me : NHAc : OMe : NO_2 = 1 : 3 : 4 : 6],$$

prepared by nitrating acetamidoparacresyl methyl ether (compare Limpach, this vol., p. 499) with acid of sp. gr. 1·48, crystallises from dilute alcohol in small needles melting at 156°.

Nitramidoparacresyl methyl ether, prepared by boiling the preceding compound with potash, crystallises in yellow needles melting at 132°. The *diamido*-derivative is obtained when the nitro-compound is reduced with tin and hydrochloric acid. It is a colourless, crystalline compound, melting at 166° with decomposition, and the aqueous solution quickly turns green on exposure to the air. The *hydrochloride*, $C_8H_{12}N_2O,2HCl$, yields an indophenol when treated with an alkaline solution of α-naphthol. The diamido-compound is, therefore, a paradiamine, and has the constitution $[Me : (NH_2)_2 : OMe = 1 : 3 : 6 : 4]$.

Orthamidoparacresyl methyl ether, $[Me : OMe : NH_2 = 1 : 4 : 6]$, is obtained by diazotising nitramidoparacresyl methyl ether and reducing the product; it melts at 111°.

F. S. K.

Action of Sulphuric Acid on γ- and δ-Isatropic Acids. By C. Liebermann and O. Bergami (*Ber.*, **22**, 782—786; compare this vol., p. 395).—Sulpho-γ-isatropic acid *a* (*α-sulphotruxillic acid a*) and the sulphonic acid of δ-isatropic acid (*β-truxillic acid*) do not reduce cold potassium permanganate at all or only do so very slowly, and both the neutral and acid barium salts, except the acid salt of α-truxillic acid *a*, are readily soluble in cold water. Meta- and parasulphocinnamic acid, with which these acids are isomeric, reduce potassium permanganate very readily in the cold, and the neutral and acid barium salts are sparingly soluble in cold water.

α-Sulphotruxillic acid *a* and β-sulphotruxillic acid are readily converted into parahydroxybenzoic acid when melted with potash.

Hydroxytruxillic acid, $(OH\cdot C_6H_4\cdot CH{:}CH\cdot COOH)_n$, is obtained when sodium α-sulphotruxillate (1 part) is mixed with melted potash (4 to 5 parts) and the temperature raised until the mass becomes bright yellow, heating being continued only until frothing has ceased. It crystallises from boiling water in colourless, anhydrous prisms, melts at 273°, and is readily soluble in alcohol, ether, and hot water, but only sparingly in cold water. Ferric chloride produces after some time a yellowish precipitate in aqueous solutions of the acid. The *barium* salt is soluble in water. Lead and silver salts produce a white precipitate in aqueous solutions of the ammonium salt. Hydroxytruxillic acid is probably a polymeride of parahydroxycinnamic acid.

Truxone, $(C_9H_6O)_n$, is precipitated when α-truxillic acid is dissolved in fuming sulphuric acid of sp. gr. 1·94 (20 parts) and the solution poured into water. It is insoluble in water, acids, and alkalis, and only very sparingly soluble in any ordinary solvent, but it separates from glacial acetic acid, xylene, or cumene in crystals melting at 289°. It dissolves in boiling nitric acid of sp. gr. 1·38 and separates unchanged, on cooling, in long, shining needles which become opaque when washed with water. It is not acted on when boiled for half an hour with a glacial acetic acid solution of chromic acid. The chloroderivative, $(C_9H_6Cl_2)_n$, prepared by treating truxone with phosphoric chloride, crystallises from benzene in colourless needles, melts at 178°, and is readily soluble in alcohol and glacial acetic acid. The *anilide*, $(C_9H_6{:}NPh)_n$, separates in yellowish needles when truxone is boiled with aniline and glacial acetic acid. It melts at 270° with decomposition, and is moderately soluble in xylene and cumene, but only very sparingly in alcohol, ether, benzene, and glacial acetic acid. The *hydrazide*, $(C_9H_6{:}N_2HPh)_n$, prepared in like manner, crystallises in small, yellow needles, melts at 270°, and resembles the preceding compound in its behaviour towards solvents.

Truxene, $(C_9H_6)_n$, is obtained, together with a small quantity of a compound of lower melting point when truxone is heated at 180° with amorphous phosphorus and hydriodic acid of sp. gr. 1·7 (6 to 7 parts); the product remains with the phosphorus and is extracted with boiling cumene, from which it crystallises in yellowish needles or plates melting above 360°. It is soluble in chloroform, boiling cumene, and boiling aniline, but insoluble in all other solvents, even in cold, concentrated sulphuric acid or boiling nitric acid of sp. gr. 1·38.

Truxenequinone, prepared by boiling truxene with chromic acid in glacial acetic acid solution, crystallises from cumene or aniline in canary-yellow needles which do not melt below 360°. It dissolves in concentrated sulphuric acid, but is reprecipitated unchanged on adding water. F. S. K.

Conversion of some Homologues of Phenol into Primary and Secondary Amines. By R. LLOYD (*Chem. News*, 59, 185—188).—When 20 grams of isobutylphenol is heated in a closed tube at 320—330° for 40 hours with 60 grams of zinc ammonium bromide and 20 grams of ammonium bromide, about 33 per cent. is converted into paramidoisobutylbenzene, about 23 per cent. into *di-isobutylphenylamine*, and about 40 per cent. remains unaltered. Paramidoisobutylbenzene (Abstr., 1881, 898), prepared from aniline, hydrochloric acid, and isobutyl alcohol, is a light-brown oil which boils at 230—231°, and yields an acetyl-derivative crystallising from warm alcohol in satiny leaflets melting at 170°. *Di-isobutylphenylamine*, $NH(C_6H_4{\cdot}C_4H_9)_2$, is a colourless oil boiling at 305—315° (decomposition sets in at 315°). Nitric acid added to the solution in concentrated sulphuric acid gives a violet coloration, becoming rapidly blue and ultimately bluish-black. The *platinochloride* forms golden needles, the *acetyl*-derivative crystallises in glistening, white leaflets, melts at 750°, and is sparingly soluble in hot water, readily in alcohol and benzene. Isoamylphenol, when treated in a similar manner, yields similar proportions of Calm's *amidoisoamylbenzene* and *di-isoamylphenylamine*. The *benzoyl*-derivative of the former crystallises in nacreous leaflets and melts at 148·5° (Calm gave 146—149°, Abstr., 1882, 1284). The *platinochloride* crystallises in golden needles. *Di-isoamylphenylamine*, $NH(C_6H_4{\cdot}C_5H_{11})_2$, is an almost colourless oil which boils at 319—321°, and discolours in the air; the golden-yellow solution in concentrated sulphuric acid also darkens in the air, and acquires first a violet then a deep-blue colour when a nitrite or nitric acid is added to it. The *platinochloride* is a compact, dark-golden, slightly crystalline substance sparingly soluble in hot alcohol. The *acetyl*-derivative crystallises from hot benzene in shining, white leaflets, melts at 81°, and is readily soluble in warm benzene and chloroform, and in hot absolute alcohol. D. A. L.

Diamidophenyl Thiocyanate. By P. T. AUSTEN (*Amer. Chem. J.*, **11**, 82—83).—The *stannous chloride compound* of this substance is obtained in clusters of lustrous needles when dinitrophenyl thiocyanate (Abstr., 1886, 693) is heated with tin and hydrochloric acid. Attempts to prepare a hydrochloride from this salt failed, but *diamidophenyl thiocyanate* was obtained from it by precipitating the tin with hydrogen sulphide, neutralising with sodium hydroxide, and evaporating; it forms pinkish-grey needles carbonising at 180° (uncorr.). A. G. B.

Oxidation-product of Triamidobenzene. By E. MÜLLER (*Ber.*, **22**, 856—859).—The *acetate* of a base, $C_{12}H_{11}N_5$, separates in long, green needles when triamidobenzene hydrochloride (10 grams) and sodium acetate (about 18 grams) are dissolved in water (200 c.c.), and a stream of oxygen passed for 2—3 hours through the warm solution (compare Nietzki and Müller, this vol., p. 604). The free *base* crystallises from hot alcohol and water, in which it is moderately easily soluble, in long, brown needles, and is decomposed when heated above

100°. The aqueous and alcoholic solutions show a yellow fluorescence. It is only a feeble base, but it dissolves in glacial acetic acid with a red coloration, and in concentrated sulphuric acid yielding a yellow solution which, when diluted, passes through violet and red, and finally becomes yellow. The *acetyl*-derivative, $C_{12}H_8N_5Ac_3$, crystallises from alcohol. The *nitrate*, $C_{12}H_{11}N_5,2HNO_3 + 2H_2O$, crystallises in long, green needles. The salts dissolve in water and alcohol, forming magenta-red solutions which show a yellow fluorescence, but on diluting, the colour suddenly changes to yellow. Dilute solutions dye wool and silk a rose-red shade, which is turned violet or blue by traces of acids, and yellow by alkalis. F. S. K.

Reduction-products of Metanitrotoluene. By K. BUCHKA and F. SCHACHTEBECK (*Ber.*, **22**, 834—842).—*Metazoxytoluene*,

$$ON_2(C_6H_4Me)_2\ [N:Me = 1:3],$$

is obtained when metanitrotoluene is boiled for six hours with a 10 per cent. solution of potash in methyl alcohol, the unchanged nitro-compound distilled with steam, and the residue extracted with ether. It crystallises from ether in bright-yellow needles, melts at 37—39°, and is readily soluble in alcohol, ether, chloroform, carbon bisulphide, and light petroleum. When distilled with iron filings, it is converted into metazotoluene (m. p. 54—55°). (Compare Barsilowsky, Abstr., 1878, 300; and Goldschmidt, Abstr., 1879, 235.)

Dinitrometazotoluene, $C_{14}H_{12}N_2(NO_2)_2$, prepared by nitrating metazotoluene at a temperature below 30° with nitric acid of sp. gr. 1·45, crystallises from glacial acetic acid in small, red needles melting at 192—193°. A mononitro-derivative seems to be formed at the same time; this compound separates from glacial acetic acid in large crystals, melts at 192—195°, and is more readily soluble in nitric acid and in glacial acetic acid than the dinitro-compound.

Metatolidine (compare Barsilowsky, *loc. cit.*, and Goldschmidt, *loc. cit.*) is best prepared by boiling metanitrotoluene with zinc-dust and alcoholic soda until metazotoluene is formed, evaporating the solution, treating the residue with cold, dilute hydrochloric acid to remove the zinc, and reducing the residual metazotoluene with hydrogen sulphide in alcoholic ammonia solution; the solution is acidified, the alcohol evaporated, and the filtered solution concentrated, whereon *metatolidine hydrochloride* separates in shining plates which gradually become blue on exposure to the air. The free base, prepared by decomposing the salt with ammonia, is a crystalline compound melting at 108—109° (compare Goldschmidt, *loc. cit.*). Aqueous solutions of the salts turn violet when heated or when treated with ferric chloride. The *diacetyl*-derivative, $NHAc\cdot C_6H_3Me\cdot C_6H_3Me\cdot NHAc$, is a light-yellow, crystalline compound melting at 274—275°.

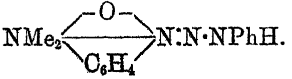
Nitrotoluene can be converted into metatoluidine boiling at 199—202°, by treating it either with tin and hydrochloric acid or with stannous chloride and hydrochloric acid, and in both cases it is completely reduced. (Compare Barsilowsky, *loc. cit.*, and Goldschmidt, *loc. cit.*)

Phenylmetatolylcarbamide, $NHPh{\cdot}CO{\cdot}NHC_7H_7$, prepared by treating phenyl isocyanate with metatoluidine in ethereal solution, crystallises from hot alcohol in colourless needles melting at 165°.

Metatolylhydrazine, $C_6H_4Me{\cdot}N_2H_3$, prepared from metatoluidine by Meyer and Lecco's method (Abstr., 1884, 597), is a light-brown oil; it boils at 240—244°, and reduces Fehling's solution; the *hydrochloride*, $C_7H_{10}N_2,HCl$, crystallises in colourless needles, and is readily soluble in alcohol and water.

Metacyanotoluene (compare Weith and Landolt, this Journal, 1875, 1194), prepared from metatoluidine by Sandmeyer's method, boils at 208—210°, and is converted into metatoluic acid when heated with 75 per cent. sulphuric acid. F. S. K.

Action of Nitroso-bases on Phenylhydrazine. By O. FISCHER and L. WACKER (*Ber.*, **22**, 622—625; compare Abstr., 1888, 1286).—When diazobenzenenitrosodimethylaniline is heated with dilute sulphuric acid and water at 100°, nitrogen is evolved and phenol nitrosodimethylaniline and dimethylparaphenylenediamine are formed. Diazobenzenenitrosodimethylaniline has most probably the constitution



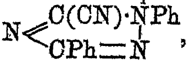
$NMe_2{<}\begin{array}{c}-O-\\ C_6H_4\end{array}{>}N{:}N{\cdot}NPhH$.

The *phenylmethylhydrazone* of nitrosoaniline, $C_{13}H_{14}N_4O$, crystallises from alcohol in slender, yellow needles, melts at 151°, and explodes when further heated. It resembles diazobenzenenitrosoaniline in its properties, but is without action on chloroform even at the boiling point.

The *phenylmethylhydrazone* of nitrosodimethylaniline, $C_{15}H_{18}N_4O$, crystallises from alcohol in thick, lustrous prisms and melts at 141°. It is without action on boiling chloroform. W. P. W.

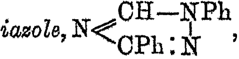
Compounds derived from Dicyanophenylhydrazine. By J. A. BLADIN (*Ber.*, **22**, 796—802; compare Abstr., 1887, 138).—*Benzylidenedicyanophenylhydrazine*, $NH{:}C(CN){\cdot}NPh{\cdot}N{:}CHPh$, is formed, together with diphenylcyanotriazole, when an alcoholic solution of dicyanophenylhydrazine is boiled for a short time with excess of benzaldehyde. The benzaldehyde and benzoic acid are removed by repeatedly evaporating with alcohol, and the residual products are isolated by repeatedly recrystallising from cold alcohol and separating the crystals mechanically, or by dissolving in benzene and precipitating the benzylidene-derivative with light petroleum. Benzylidenedicyanophenylhydrazine is very readily soluble in alcohol, from which it crystallises in small, light-yellow, prismatic needles melting at 129—129·5°. It is insoluble in water, but readily soluble in ether and benzene, and is precipitated from the benzene solution in microscopic needles on adding light petroleum. When boiled with hydrochloric acid in alcoholic solution, it yields benzaldehyde, and when oxidised, it is converted into diphenylcyanotriazole.

Diphenylcyanotriazole,



$N{<}\begin{array}{l}C(CN){\cdot}NPh\\ CPh{=}N\end{array}$, remains in solution when light petroleum is added to a benzene solution of the crude product obtained as described above, and it can also be prepared by oxidising the preceding compound with ferric chloride or silver nitrate. It crystallises from a mixture of benzene and light petroleum in small, colourless needles, melts at 156—156·5°, and is readily soluble in benzene, ether, and alcohol, but only very sparingly in light petroleum, and is insoluble in water.

Diphenyltriazolecarboxylic acid, $C_{15}H_{11}N_3O_3$, is obtained when diphenylcyanotriazole or benzylidenedicyanophenylhydrazine is boiled with alcoholic potash and the filtered solution acidified with hydrochloric acid. It is best prepared by boiling the crude product of the action of benzaldehyde on dicyanophenylhydrazine with alcoholic potash, dissolving the crude acid in alcoholic ammonia, evaporating the alcohol, and precipitating the acid from the filtered solution. It is almost insoluble in water, and only moderately soluble in ether, but dissolves freely in alcohol, from which it separates in colourless crystals containing 1 mol. of alcohol. The crystals lose their alcohol at 100°, and have no well-defined melting point, being decomposed, with evolution of gas, at temperatures ranging from 172° to 182°. The *methyl* salt, $C_{16}H_{13}N_3O_2$, prepared from the silver salt, crystallises from methyl alcohol in colourless needles melting at 159°, and is moderately soluble in ether, but insoluble in water. The *ethyl* salt, $C_{17}H_{15}N_3O_2$, prepared in like manner, crystallises from alcohol in colourless needles melting at 164—165°, and is only sparingly soluble in ether, and insoluble in water. The alkaline salts are very readily soluble in water. The *calcium*, *barium*, and *copper* salts are amorphous. The *silver* salt, $C_{15}H_{10}N_3O_3Ag$, is sparingly soluble in water. The *amide*, $C_{15}H_{12}N_4O$, is obtained when diphenylcyanotriazole or benzylidenedicyanophenylhydrazine is dissolved in warm alcohol and the solution heated for a short time with a 3 per cent. solution of hydrogen peroxide and a few drops of potash. It is readily soluble in alcohol, but only sparingly in water, from which it separates in small, slender needles melting at 195—196°.

Diphenyltriazole,  $N\!<\!\begin{matrix}CH—NPh\\ \vert \\ CPh:N\end{matrix}$, was prepared, but only in an impure condition, by heating the carboxylic acid above its melting point. It is a very feeble base, readily soluble in benzene and alcohol, but more sparingly in ether, and insoluble in water. F. S. K.

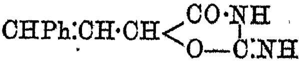
Benzyl-derivatives of Hydroxylamine. By R. Behrend and K. Leuchs (*Ber.*, **22**, 613—618; compare this vol., p. 500).—When hydroxylamine hydrochloride (2 mols.) and benzyl chloride (3 mols.) react in alcoholic solution in the presence of sodium carbonate, an oil is obtained from which dibenzylhydroxylamine in the form of its hydrochloride can be extracted with water. From the residual oil, ether extracts tribenzylhydroxylamine and an oil destitute of basic properties, and the former can be separated from the solution in the form of its *platinochloride*, $[(C_7H_7)_3NO]_2,H_2PtCl_6$, which crystallises in characteristic forms showing prism and dome faces, melts at 155—157° with decomposition, and is sparingly soluble in alcohol.

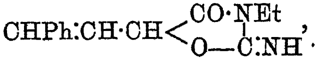
Tribenzylhydroxylamine, obtained in this way, is an oil which, when heated at 160° with concentrated hydrochloric acid, yields noteworthy quantities of the dibenzylhydroxylamine (m. p. 123°) together with other decomposition products: its *hydrochloride* crystallises in needles, melts at 91°, and is decomposed by water, and its *picrate* is very sparingly soluble in alcohol, and melts at 131—132°. From the ethereal filtrate from the platinochloride, an oil is obtained which seems to have the composition of a tribenzylhydroxylamine (*loc. cit.*), but is destitute of basic properties.

The oily α-dibenzylhydroxylamine, $C_7H_7{\cdot}NH{\cdot}OC_7H_7$ (*loc. cit.*), when heated with hydrochloric acid at 130°, decomposes into benzyl chloride, and the hydrochloride of Beckmann's β-benzylhydroxylamine (this vol., p. 608), to which the authors assign the constitution $C_7H_7{\cdot}NH{\cdot}OH$ on the assumption that in hydroxylamine the benzyl-group is substituted for "hydroxylic" hydrogen in those benzylhydroxylamines which do, and for "non-hydroxylic" hydrogen in those which do not yield benzyl chloride when heated with hydrochloric acid. W. P. W.

Methylacetanilide. By H. GIRAUD (*Compt. rend.*, **108**, 749—750). —Under the name *exalgine*, Dujardin-Beaumetz has recently described a new medicine (*Compt. rend.*, **108**) which is said to be orthomethylacetanilide, capable of existing in three modifications. The name orthomethylacetanilide can, however, only be applied to the acetorthotoluide of Beilstein and Kuhlberg; whilst exalgine is the methylacetanilide which was described by Hofmann in 1874, and is made on a large scale for the preparation of monomethylaniline. It does not form isomeric modifications. C. H. B.

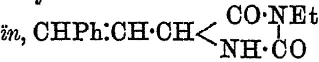
Hydantoïns. By A. PINNER and A. SPILKER (*Ber.*, **22**, 685—698). —Cinnamylhydantoïn (cinnamylmetapyrazolone, Pinner and Lifschütz, Abstr., 1887, 1055) is prepared by diluting 250 grams of crude cinnamon oil (*oleum Cassiæ rect.*) with an equal weight of ether, and adding the whole to finely-powdered 96 per cent. potassium cyanide (220 grams) previously treated with an equal weight of water. It is then cooled with ice, and treated with 37 per cent. hydrochloric acid (330 grams), which is added in small portions, the whole being violently shaken all the time. It is kept for 12 hours at the ordinary temperature, during which time it is continually shaken, and the ether separated, and evaporated at the ordinary temperature. The residue is kept for 10 days over sulphuric acid and potash, the crystals which separate freed from adhering oil by suction, and then washed with a mixture of benzene and light petroleum. 370 grams of sufficiently pure cinnamaldehyde hydrocyanide is obtained from 500 grams of cinnamon oil. The hydrocyanide (3 parts) is heated with finely-powdered urea for $2\frac{1}{2}$ hours on a water-bath, the product washed with ether, and saponified with hydrochloric acid.

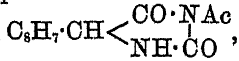
Cinnamylpseudohydantoïn,  $CHPh{:}CH{\cdot}CH{<}\begin{matrix}CO{\cdot}NH\\ \vert\\ O{-}C{:}NH\end{matrix}$, is obtained by heating the above compound (not continuously) for 12 hours with solution of potash (2 mols.) in absolute alcohol. The product is treated with an equal volume of water, precipitated with acetic acid, and crystallised from glacial acetic acid. It crystallises in small needles of a silky lustre, decomposes at 300°, dissolves very sparingly in glacial acetic acid and alcohol, is almost insoluble in ether, benzene, and chloroform, readily soluble in alkalis. The *ethyl salt*,



$$\mathrm{CHPh{:}CH{\cdot}CH}<\begin{array}{l}\mathrm{CO{\cdot}NEt}\\ \quad\;\;|\\ \mathrm{O{-}C{:}NH}\end{array},$$

prepared by heating the pseudohydantoïn with potash dissolved in 80 per cent. alcohol and an excess of ethyl bromide for five hours at 100°, melts at 280°, and is very sparingly soluble. When heated with strong aqueous baryta at 100° in a closed tube, α-hydroxycrotonic acid (Matsmoto, *Ber.*, 8, 1145; Peine, Abstr., 1884, 1344), ethylamine, ammonia, and carbonic anhydride are formed.

Ethylcinnamylhydantoïn,  $\mathrm{CHPh{:}CH{\cdot}CH}<\begin{array}{l}\mathrm{CO{\cdot}NEt}\\ \quad\;\;|\\ \mathrm{NH{\cdot}CO}\end{array}$, is formed when either of the cinnamylhydantoïns (m. p. 172° or m. p. 198°) are heated with alcoholic potash and ethyl bromide at 100°. It melts at 162°, is very readily soluble in alcohol, rather readily in ether and benzene, sparingly in water. It is decomposed by baryta with formation of phenyl-α-amidocrotonic acid, ethylamine, and carbonic anhydride. *Phenyl-α-amidocrotonic acid*, $C_{10}H_{11}NO_2$, is a white powder; it melts at 240—250°, and is sparingly soluble in alcohol and water; the *barium salt* crystallises well, and is readily soluble; its *silver salt* forms very sparingly soluble, microscopic needles.

Acetylcinnamylhydantoïn,  $\mathrm{C_8H_7{\cdot}CH}<\begin{array}{l}\mathrm{CO{\cdot}NAc}\\ \quad\;\;|\\ \mathrm{NH{\cdot}CO}\end{array}$, crystallises in small, white prisms, melts at 185°, dissolves readily in alcohol, rather sparingly in water. The same compound is obtained from both cinnamylhydantoïns; no crystalline acetyl compound could be obtained from the pseudohydantoïn.

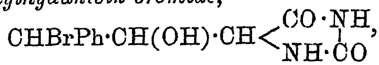
Cinnamylhydantoïnamide, $\mathrm{CHPh{:}CH{\cdot}CH(CONH_2){\cdot}NH{\cdot}CONH_2}$, is readily obtained when phenylcrotonitrilecarbamide is dissolved in sulphuric acid (10 parts) at 0°, kept for 24 hours at the ordinary temperature, and then slowly poured on to ice (50 parts). The precipitate is repeatedly dissolved in slightly ammoniacal water. It is a microcrystalline powder, melts at 210—220° with evolution of ammonia, dissolves readily in alcohol, sparingly in hot water. When boiled with an equivalent amount of alkali, *hydantoic acid*, $C_{11}H_{12}N_2O_3$, is formed. This crystallises in plates, melts at 185°, and is readily soluble in alcohol and hot water. When the amide is heated with dilute acids, the hydantoïn melting at 172° is formed.

Cinnamylhydantoïn dibromide, $C_{11}H_{10}N_2O_2Br_2$, prepared by adding bromine diluted with chloroform to cinnamylhydantoïn dissolved in boiling chloroform, care being taken to exclude every trace of water, is a sparingly soluble powder which melts at 198—200° with decomposition. When boiled with water, cinnamylhydantoïnhydroxybromide is formed.

Cinnamylpseudohydantoïn dibromide, $C_{11}H_{10}N_2O_2Br_2$, melts at 250°

with decomposition, and is sparingly soluble in benzene and chloroform.

Hydroxycinnamylhydantoïn bromide,



$$\mathrm{CHBrPh{\cdot}CH(OH){\cdot}CH}{<}\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \quad\ \ |\\ \mathrm{NH{\cdot}CO}\end{array},$$

is formed when bromine-water is added to an alcoholic or aqueous solution of cinnamylhydantoïn. It melts at 223° with decomposition, and is rather readily soluble in alcohol. When heated for five minutes with the equivalent amount of aqueous soda, and acidified with acetic acid, *hydroxycinnamylhydantoïn*, $\mathrm{CHPh{:}C(OH){\cdot}CH{\cdot}C_2N_2O_2H_2}$, is obtained. This melts at 185° with decomposition, dissolves readily in alcohol and ether, hardly at all in water.

Ethoxycinnamylhydantoïn bromide, $\mathrm{CHBrPh{\cdot}CH(OEt){\cdot}CH{\cdot}C_2N_2O_2H_2}$, is prepared by adding dry bromine to a cold absolute alcoholic solution of cinnamylhydantoïn, and precipitating with water. It crystallises in small, white prisms, melts at 175° with decomposition, and dissolves readily in alcohol and ether, less so in chloroform and benzene.

Ethylisobutylhydantoïn, $\mathrm{CHBu}{<}\begin{array}{l}\mathrm{CO{\cdot}CEt}\\ \quad\ \ |\\ \mathrm{NH{\cdot}NO}\end{array}$, prepared by heating isobutylhydantoïn with the equivalent amounts of potash and ethyl bromide at 100°, crystallises in white needles of a silky lustre, melts at 135°, boils at 295°, and is readily soluble in alcohol, ether, and hot water.

Isobutylhydantoic acid, $\mathrm{COOH{\cdot}CHBu{\cdot}NH{\cdot}CONH_2}$, is obtained by boiling the hydantoïn for three hours with aqueous baryta (2 parts), precipitating the excess of baryta with carbonic anhydride, and acidifying with acetic acid. It crystallises in long needles, melts with effervescence at 200°, and dissolves readily in alcohol and hot water. The *barium salt* forms readily soluble prisms.

When isobutylhydantoïn is heated with an excess of baryta in a closed tube at 100, isobutylamidoacetic acid (Limpricht, Hüfner) is formed. This crystallises in plates which melt at 210—220° in an open tube, and at 270° in a closed tube.

Isobutylhydatoinamide, $\mathrm{CONH_2{\cdot}CHBu{\cdot}NH{\cdot}CONH_2}$, is formed when the crude carbamide-derivative of valeraldehyde hydrocyanide is carefully added to strong sulphuric acid (8 parts) at 0°. After being kept for some days at the ordinary temperature, it is dropped on to ice (5 parts), carefully avoiding a rise of temperature above 0°. The solution is then added to the calculated amount of alcoholic ammonia cooled to 0°. Nearly all the ammonium sulphate is precipitated by further addition of alcohol, and the filtrate from this is evaporated at a low temperature, and finally in a vacuum. The amide is crystallised from a little hot water. It melts at 170° with decomposition, and is readily soluble. Boiling dilute acid and alkali convert it respectively into the hydantoïn and the hydantoic acid.

Phenylhydantoic amide, $\mathrm{CONH_2{\cdot}CHPh{\cdot}NH{\cdot}CONH_2}$, prepared by the action of cold strong sulphuric acid on the carbamide-derivative of benzaldehyde hydrocyanide, crystallises in very lustrous prisms, melts at 223° with decomposition into hydantoïn and ammonia, and is readily soluble in water and alcohol, less so in ether and benzene.

Acetylphenylpseudohydantoïn is obtained in crystals by keeping the product of the action of acetic anhydride on pseudophenylhydantoïn (Abstr., 1888, 1102) for some months. It forms small prisms, decomposes at about 290°, and dissolves readily in glacial acetic acid and in alkalis, sparingly in alcohol. N. H. M.

Action of Alkalis and Ammonia on Halogen-substituted Quinones. By F. KEHRMANN (*J. pr. Chem.* [2], **39**, 318—320).—*Paradiethoxydichloroquinone*, $C_6O_2Cl_2(OEt)_2$, is obtained as follows:—Sublimed and powdered chloranil is mixed with 25—30 times its weight of alcohol (96 per cent.) heated to 50°, and alcoholic potash (1 per cent.) dropped in. The mixture is then heated, and half its bulk of hot water added, filtered whilst hot, allowed to crystallise, and recrystallised from alcohol. It crystallises in large, garnet-red, four-sided tables easily soluble except in water. Potash converts it into potassium chloranilate. Ammonia colours its alcoholic solution red, and forms brownish-violet needles of an amido-derivative, which colours alkalis an intense but fugitive blue. Hydrochloric acid and tin decolorise its ethereal solution, forming *dichlorodiethoxyquinol*, $C_6Cl_2(OH)_2(OEt)_2$, which forms large, colourless tables melting at 148—150°, and freely soluble except in water.

Dimethoxydichloroquinone is obtained if potash dissolved in methyl alcohol is used in the above prescription; it forms garnet-red crystals melting at 130°, and less soluble than the ethoxy-compound. The corresponding *quinol* has been obtained. A. G. B.

Reissert's Anilosuccinic Acid and Anilopropionic Acid. Oxanilic Acid. By R. ANSCHÜTZ (*Ber.*, **22**, 731—748).—Reissert (Abstr., 1888, 694, 954) described an acid which he called pyranilpyroic acid (γ-ketotetrahydroquinaldinecarboxylic acid), and stated that on oxidation it yielded γ-keto-α-hydroxytetrahydroquinoline-α-carboxylic acid, a statement which he subsequently altered, and assigned to the oxidation-product the constitution of an anilosuccinic acid, $COOH{\cdot}CH_2{\cdot}C(NPh){\cdot}COOH$. This last-named acid is, according to Reissert, readily decomposed by water into oxalic acid and acetic acid. The author has previously shown that judging from the method of formation, properties, and decomposition-products of the so-called pyranilpyroic acid, it is the anil of a mesaconic acid, and, relying on Reissert's statement regarding the decomposition of the so-called anilosuccinic acid, he suggested that the latter was probably oxanilacetic acid, $NHPh{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}COOH$. In order to test Reissert's results experimentally, the author oxidised mesaconilic acid (pyranilpyroic acid) exactly as described by Reissert, as far as was possible from the latter's description, and proved that oxanilic acid, oxalic acid, carbonic anhydride, and a small quantity of an indifferent compound melting at 188° are formed, and, further, that the so-called anilosuccinic acid is in reality oxanilic acid, and does not yield acetic acid when decomposed. The oxidation of mesaconilic acid is, therefore, of no value in determining its constitution.

Reissert's work is severely criticised throughout. F. S. K.

Substituted Glycine Anhydrides. By E. Erlenmeyer, Jun. (*Ber.*, **22**, 792—795).—Hippuric acid and phthalic anhydride react very readily when warmed together in presence of sodium acetate and acetic anhydride, yielding a compound, $C_{34}H_{18}N_2O_8$. The product obtained in like manner from hippuric acid and benzaldehyde has the composition $C_{32}H_{22}N_2O_4$.

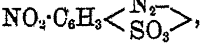
The condensation products of hippuric acid are nearly related to glycine anhydride (compare Curtius and Goebel, Abstr., 1888, 576), which itself shows a certain analogy with pseudoindoxyl. This last-named fact may account for the readiness with which hippuric acid combines with aldehydes, &c., and perhaps it is a general rule that methylene-groups situated between a carboxyl radicle and a nitrogen-atom react readily with aldehydes. F. S. K.

Three Isomeric Toluric Acids; Behaviour of Metaxylene in the Animal System. By A. Gleditsch and H. Moeller (*Annalen*, **250**, 376—380).—Ortho-, meta-, and para-toluric acids are obtained by acting on the chlorides of the corresponding toluic acids with glycocine and an excess of sodium hydroxide. *Orthotoluric acid* crystallises in thick plates soluble in water. It melts at 162·5°. The para-acid (Kraut, *ibid.*, **98**, 360) is deposited from water in glistening plates soluble in alcohol and in hot water. It melts at 161—161·5°. *Metatoluric acid* melts at 139°, and is more soluble in water than the para-acid. The three toluric acids can also be obtained from the urine of animals to which doses of the three isomeric toluic acids have been administered. In the organism of the dog, metaxylene is converted into metatoluric acid (m. p. 138·5°), not into a liquid toluric acid, as stated by Schultzen and Naunyn (*Arch. Physiol. Anat.*, 1867, 349). W. C. W.

Ethyl Benzylcyanosuccinate. By L. Barthe (*Compt. rend.*, **108**, 816—817).—This compound was obtained by the action of benzyl chloride on an alcoholic solution of the sodium-derivative of ethyl cyanosuccinate. It forms a colourless, viscous liquid, which boils at 220—228° under a pressure of 18—20 mm., and does not crystallise at −15°. The yield of ethyl benzylcyanosuccinate is slightly greater than the weight of ethyl cyanosuccinate taken.

C. H. B.

Derivatives of Paranitrometamidobenzenesulphonic Acid. By E. Eger (*Ber.*, **22**, 847—852).—*Diazonitrobenzenesulphonic acid*,



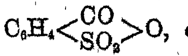
$NO_2{\cdot}C_6H_3{<}\begin{matrix}N_2—\\SO_3\end{matrix}{>}$, separates in long, yellow needles, when a 49 per cent. solution of sodium nitrite (4·2 c.c.) is added to a well-cooled aqueous solution of paranitrometamidobenzenesulphonic acid (6·6 grams), and the mixture kept for some time. It crystallises with water, explodes violently when heated, and combines with Schäffer's β-naphtholsulphonic acid, yielding a bright orange compound.

A ruby-red *azo*-dye, $SO_3Na{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, is obtained when the preceding compound is treated with β-naphthol. It dissolves in soda with a violet coloration, but on adding dilute acetic acid, it is precipitated in shining green and red dichroic, hygroscopic plates. Paraphenylenediaminesulphonic acid (compare Griess, Abstr., 1883, 180), prepared by reducing nitramidobenzenesulphonic acid with stannous chloride and hydrochloric acid, crystallises from dilute sulphuric acid in anhydrous, colourless needles, is readily soluble in hydrochloric acid, moderately so in water, sparingly in dilute alcohol, and insoluble in ether and benzene. It turns green on exposure to the air, or when dried at a moderate temperature.

When amidoazobenzenesulphonic acid, prepared from "acid-" or "fast-yellow" (compare Grässler, D.R.-P., No. 4186), is reduced with the calculated quantity of stannous chloride and hydrochloric acid, it yields sulphanilic acid and paraphenylenediaminesulphonic acid. If "acid-yellow" is diazotised as described by Grässler (*loc. cit.*), and the diazo-compound boiled with alcohol, an azobenzenedisulphonic acid, identical with the acid prepared by Limpricht (Abstr., 1882, 1197) and Rodatz (*Annalen*, **215**, 213), is obtained.

The amidoazobenzenedisulphonic acid which, together with the corresponding monosulphonic acid, constitute "acid-yellow," has therefore the constitution [$SO_3H : N : N : SO_3H = 3' : 1' : 1 : 4$], and, when reduced with stannous chloride and hydrochloric acid, it seems to be converted into a diphenylenedisulphonic acid. F. S. K.

Sulphobenzoic Acid and its Derivatives. By C. FAHLBERG and R. BARGE (*Ber.*, **22**, 754—767).—When benzoicsulphinide is evaporated to dryness with excess of hydrochloric acid until the sweet taste goes, the residue consists entirely of ammonium hydrogen orthosulphobenzoate, $COOH\cdot C_6H_4\cdot SO_3NH_4$, and not of the free acid, as stated by Brackett and Hayes (Abstr. 1888, 279). As therefore Bracket and Hayes never had the free acid in their hands, their analyses and conclusions are erroneous.

Orthosulphobenzoic acid, $COOH\cdot C_6H_4\cdot SO_3H$, can be obtained by decomposing the silver salt, prepared by precipitating a concentrated solution of the ammonium salt (1 mol.) with silver nitrate (2 mols.), with hydrochloric acid or hydrogen sulphide, and evaporating the filtered solution; it can also be prepared by decomposing any neutral or acid salt with excess of warm, concentrated sulphuric acid. It crystallises in prisms with 3 mols. H_2O, loses about half its water at 100°, and is decomposed at 100—105°. It is readily soluble in water and alcohol, but insoluble in ether. The *anhydride*,  $C_6H_4<^{CO}_{SO_2}>O$, can be prepared by treating the acid with acetic chloride, or by heating the potassium salt with phosphoric chloride at 180°. It crystallises from benzene or ether in large, monoclinic prisms, melts at 118—119°, and is very readily decomposed by water.

Ammonium orthobenzaminesulphonate, $NH_2\cdot CO\cdot C_6H_4\cdot SO_3NH_4$, separates when anhydrous ammonia is passed into a hot benzene solution of the anhydride. It crystallises from alcohol in slender, colourless needles, melts at 255—256°, and is readily soluble in water; it does not taste sweet, and when boiled with dilute alkali, ammonia is evolved. When heated at 170° with concentrated hydrochloric acid, it is converted into the ammonium hydrogen salt of orthosulphobenzoic acid, and when heated alone it is decomposed in a similar manner to ammonium orthosulphobenzoate. The *silver* salt,

$$NH_2\cdot CO\cdot C_6H_4\cdot SO_3Ag,$$

crystallises in plates. The free acid, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H$, prepared by decomposing the silver salt with hydrogen sulphide, separates from water in compact prismatic crystals containing $1H_2O$, and is readily soluble in alcohol and water.

Remsen and Hayes (Abstr., 1888, 153) heated resorcinol with what they thought was orthosulphobenzoic acid, but which was in reality the ammonium hydrogen salt of this acid, and obtained a compound which they named sulphofluoresceïn, and to which they assigned the composition $C_{19}H_{12}O_6S + 2H_2O$. This substance the authors find has the composition $C_{13}H_{13}O_6SN + 2H_2O$, and it is formed by the direct combination of resorcinol and the ammonium hydrogen sulphonate with elimination of 1 mol. H_2O. It forms pale-yellow crystals, and is readily soluble in water and alcohol, the dilute alkaline solutions showing a slight fluorescence. It loses the whole of its water at 120°, evolves ammonia when boiled with potash, and is converted into resorcinol and ammonium hydrogen orthosulphobenzoate when heated at 220° with concentrated hydrochloric acid. It is not hydrolysed when heated with alcoholic ammonia, or when boiled with potash or baryta, but when boiled with alcoholic potash it is converted into the salt $C_6H_3(OK)_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3K$. It is, therefore, in all probability ammonium dihydroxybenzoylbenzenesulphonate,

$$C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3NH_4,$$

in which case it would be analogous to dihydroxybenzoylbenzoic acid (compare Baeyer, *Annalen*, **183**, 23).

When orthosulphobenzoic acid (1 mol.) is heated with resorcinol (4 mols.), a compound, $C_{31}H_{20}O_8S + 4H_2O$ (*sulphofluoresceïn*), is formed; if only 2 mols. of resorcinol are employed, a considerable quantity of the acid remains unchanged. The properties and constitution of this compound will be further investigated. F. S. K.

Sulphonephthaleïns. By I. REMSEN and A. F. LINN (*Amer. Chem. J.*, **11**, 73—80).—The substance prepared by heating benzoic sulphinide with concentrated hydrochloric acid at 150°, which Remsen and Hayes (Abstr., 1888, 153) regarded as orthosulphobenzoic acid, is really *acid ammonium orthosulphobenzoate*, $COOH{\cdot}C_6H_4{\cdot}SO_3NH_4$. The substance which they obtained by heating this salt with resorcinol (*loc. cit.*) crystallises in monoclinic plates, perfectly white and not fluorescent; it is not sulphonefluoresceïn but *ammonium dihydroxybenzoylbenzenesulphonate*, $C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3NH_4$.

Dihydroxybenzoylbenzenesulphonic acid, $C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H$, crystallises in small plates (with 2 mols. H_2O) with satiny lustre, and is very soluble in water; the solution is not coloured by alkalis; at 120° it loses water, becoming yellow and finally dark brown, when it gives an intense greenish-yellow fluorescence with alkalis. The *barium salt* forms large, pale yellow, monoclinic plates.

Sulphonefluoresceïn, $C_{19}H_{12}O_6S + H_2O$, is obtained by acidifying a solution in caustic potash of the brown mass mentioned above, as a dark reddish-brown substance, sparingly soluble except in alkalis. It is still under investigation. A. G. B.

Paranitroorthosulphobenzoic Acid. By J. H. KASTLE (*Amer. Chem. J.*, **11**, 177—199).—The author has obtained this acid in quantity by oxidising in hot solution potassium paranitrotolueneorthosulphonate (10 parts) dissolved in water (500 parts) containing potash (3 parts), with potassium permanganate (22 parts). The product is cooled, filtered, evaporated, and treated with excess of hydrochloric acid, when the acid potassium salt crystallises in slender, white needles. The free acid separates from a hot aqueous solution in white needles melting at 110° to a jelly-like mass, which does not become perfectly liquid until heated to a considerably higher temperature. On heating the acid potassium salt, $NO_2·C_6H_3(SO_3H)·COOK$, at 150°, with a little more than its own weight of phosphorus pentachloride, the dichloride $NO_2·C_6H_3(SO_2Cl)·COCl$ [= 1 : 3 : 4] is obtained; this crystallises in slender yellow needles, or in elongated flat plates, which become waxy on heating, and melt at 60° to a clear liquid. The alkyl salts, obtained by the action of alcohols on this dichloride, are not analogous to those obtained by Graebe (*Ber.*, **16**, 860) in the case of phthalyl chloride, but are compounds of the order $NO_2·C_6H_3(SO_3R)·COOR$; consequently, in the dichloride one chlorine-atom is in combination with the carbonyl-group, the other with the sulphonic group. The easy formation of nitrobenzoicsulphinide from the chloride by treatment either with aqueous or gaseous ammonia, also speaks strongly in favour of this view. G. T. M.

Oxidation of Benzene-derivatives with Potassium Ferricyanide. By W. A. NOYES and W. B. WILEY (*Amer. Chem. J.*, **11**, 161—164; compare Abstr., 1886, 804).—*Paranitroorthosulphaminebenzoic acid*, the product of oxidation of paranitroorthotoluenesulphonamide with potassium ferricyanide (Abstr., 1887, 727) may be more conveniently prepared as follows:—Potash (30 grams) and potassium permanganate (8 grams) are dissolved in water (150 c.c.). The mixture is heated by passing steam through it, the amide (5 grams) is introduced and the solution shaken vigorously. A 3 per cent. solution of potassium permanganate is now added, a little at a time, until the liquid, still kept hot by means of steam being blown through it, remains green for a few minutes. Alcohol is added to reduce the last traces of manganate, the liquid is filtered, nearly neutralised with hydrochloric acid, evaporated to a small bulk, strongly acidified and extracted with ether. The acid remaining after distilling off the ether is converted into barium salt and washed with alcohol, in order to remove the remaining traces of unoxidised amide. The free acid separates from a hot aqueous solution in small, granular crystals, which if heated quickly melt at 172°, if heated slowly at 177°; if kept at the latter temperature for a short time, the fused mass solidifies, being converted into the sulphinide melting at 209°. The barium salt, $[C_6H_3(NO_2)(SO_2NH_2)·COO]_2Ba$, crystallises from hot alcohol in fine feathery needles containing 1 mol. H_2O, from water with a larger quantity of water of crystallisation. The silver salt, $C_7H_5N_2O_6Ag + \frac{1}{2}H_2O$, crystallises in short, thick, yellow needles; the salt,

$$C_6H_4N_2O_6Ag_2 + H_2O,$$

is a greenish-yellow, crystalline powder. G. T. M.

Action of Acetic Anhydride on 2′-Indolecarboxylic Acid. By C. ZATTI (*Ber.*, **22**, 661—665).—*3′-Acetylindole*, C_8H_6NAc, is obtained by heating 2′-indolecarboxylic acid (prepared by Ciamician and Zatti's method, Abstr., 1888, 957) with acetic anhydride (10 parts) at 220° for seven hours; the excess of acetic acid is distilled off under diminished pressure, the residue repeatedly extracted with water and the solution neutralised with sodium carbonate. It is then filtered, the filtrate extracted with ether and the residue obtained by evaporating the ether crystallised from boiling water and benzene. It forms small, white needles, melts at 188—190° (corr.), dissolves readily in hot water and hot benzene, and sublimes in plates. It is improbable that the compound is identical with v. Baeyer's acetylindole (Abstr., 1879, 938), which melts at 182—183°. *3′-Indoleacetoxime*, $C_8H_6N{\cdot}CMe{:}N{\cdot}OH$, crystallises in white needles melting at 144—147°. The position of the acetyl-group in acetylindole was determined by fusion with potash; the product yielded 3′-indolecarboxylic acid (Ciamician and Zatti, *loc. cit.*).

Diacetylindole, $C_{12}H_{11}NO_2$, is the sparingly soluble substance which separates from the hot aqueous extract of the crude product mentioned above. It is purified by precipitating the concentrated benzene solution with light petroleum, when it separates as a white, crystalline powder, melting at 147—150°. It dissolves sparingly in boiling water, readily in boiling benzene, and sublimes in needles. When boiled with sodium carbonate, 3′-acetylindole is formed. It is very probable that the acetyl-group so eliminated is attached to the nitrogen of the indole [$Ac_2 = 1 : 3′$].

It is suggested that v. Baeyer's acetyl-derivative, melting at 146°, may be 1′ : 2′ diacetylindole. N. H. M.

Diphenyltriketone. By H. v. PECHMANN (*Ber.*, **22**, 852—853).—*Nitrosodibenzoylmethane*, a crystalline compound melting at 146°, yields two bromo-derivatives, namely, *dibenzoylmethyl bromide*, $COPh{\cdot}CHBr{\cdot}COPh$ (m. p. 93°), and *dibenzoylmethylene bromide*, $COPh{\cdot}CBr_2{\cdot}COPh$ (m. p. 95°). The monobromide gives an *acetyl-derivative*, $COPh{\cdot}CH(OAc){\cdot}COPh$, melting at 94°, which reacts with bromine, forming the compound $COPh{\cdot}CBr(OAc){\cdot}COPh$, melting at 101·5°. The latter can also be obtained by treating the dibromide (1 mol.) with potassium acetate (1 mol.), and when heated above its melting point, alone or in solution, it is decomposed into acetic bromide and diphenyltriketone.

Diphenyltriketone, $COPh{\cdot}CO{\cdot}COPh$, forms golden-yellow crystals, melts at 69—70°, and boils above 300° without decomposition. It combines with 1 mol. H_2O, yielding a crystalline *hydrate* which melts at 90°, and at a higher temperature is reconverted into the triketone. It dissolves in dilute soda, and is thereby converted into some new compound. When shaken with concentrated sulphuric acid and benzene containing thiophen, it gives a blue coloration.

F. S. K.

Diphenyltrichlorethane and its Homologues. By K. ELBS and H. FÖRSTER (*J. pr. Chem.* [2], **39**, 298—301).—When diphenyltrichlorethane in alcoholic solution is reduced with zinc-dust and ammonia, stilbene is the chief product. Ditolyltrichlorethane treated in the same way yields paradimethylstilbene (m. p. 177°).

Metadixylyltrichlorethane, prepared from chloral and metaxylene, crystallises in white grains melting at 106°. It yields *metadixylyldichlorethylene* when heated with alcoholic potash; this forms white crystals melting at 101°.

Paradixylyltrichlorethane crystallises in white needles melting at 87°. *Paradixylyldichlorethylene*, also crystallising in white needles, melts at 95°.

When metadixylyltrichlorethane is reduced, it yields metatetramethylstilbene (m. p. 106°). A. G. B.

The Third Benziledioxime. By K. AUWERS and V. MEYER (*Ber.*, **22**, 705—720).—γ-Benziledioxime is prepared by dissolving the γ-monoxime (m. p. 113—114°) previously described as β-monoxime (this vol., p. 403) and soda (4 parts) in sufficient cold water to give a clear solution, adding hydroxylamine hydrochloride (2 parts), and keeping the whole at the ordinary temperature for a day or two, until there is no further loss of colour. It is then diluted, strongly acidified with hydrochloric acid, and the precipitate, consisting chiefly of the γ-dioxime, but containing also small amounts of the α- and αβ-compounds, is filtered, pressed, and shaken with cold alcohol (10 parts). It is then filtered and evaporated spontaneously. The white crystals are separated and recrystallised from cold alcohol, when it forms slender, lustrous needles. When a small quantity of the dried substance is heated on a water-bath, it melts, and at once solidifies to a hard, crystalline mass; when this is heated in a capillary tube, it melts at 164—166°, but again solidifies; it now melts at 200° with decomposition. This is due to the substance first losing alcohol of crystallisation, and then at the next higher melting point being converted into the β-dioxime (m. p. 207°). It dissolves very readily in the usual solvents, except water and light petroleum in which it is insoluble. When heated for several days at 100°, it is converted into the β-dioxime; the same change takes place when the alcoholic solution is boiled for some hours, or when an alkaline aqueous solution is heated in a water-bath. Strong hydrochloric acid at 100° converts it into the β-dioxime, which is then further decomposed into benzile and hydroxylamine hydrochloride. *γ-Diacetylbenziledioxime*, $C_{18}H_{16}N_2O_4$, crystallises in slender, white needles, melting at 114—115°, and is very readily soluble in benzene, carbon bisulphide, and glacial acetic acid, but less so in cold alcohol and ether, and insoluble in water. The *γ-dipropionyldioxime*, $C_{20}H_{20}N_2O_4$, melts at 86—87°, but otherwise resembles the acetyl-compound. The *γ-Diisobutyryl-compound* separates from the alcoholic solution in very lustrous, microscopic prisms, melts at 89—92°, and is readily soluble in the usual solvents, except water in which it is insoluble. When either of these three compounds is kept over night with alkali, treated with water and acidified, the anhydride of the dioxime, identical with that previously obtained both from the α- and αβ-dioxime, is formed. The reaction is of importance, as it shows that the γ-dioxime has the same constitution as its two isomerides; it also affords evidence in favour of the view that the γ-dioxime represents that configuration of benziledioxime material in which, both isonitroso-groups being attached to corresponding positions, elimination of water can readily take place. When a very dilute alcoholic solution of the γ-dioxime is treated with potassium ferricyanide (not quite 3 parts), it is converted into the compound $C_{14}H_{10}N_2O_2$, identical with that obtained by oxidation of the α- and αβ-dioximes. The molecular weight of the acetyl-derivative was determined by Raoult's method, and the numbers 299 and 303 obtained; the number required by the formula $C_{18}H_{16}N_2O_4$ is 324.

There are at present five oximes of benzile known, two monoximes, and three dioximes, and there are already indications of the existence of the third monoxime (β-benzilemonoxime).

The bearing of these results on the authors' stereo-chemical hypothesis is discussed (compare Abstr., 1888, 597). N. H. M.

Fichtelite. By E. BAMBERGER (*Ber.*, **22**, 635—637).—The specimen of fichtelite examined by the author was obtained from Kolbermoor, near Rosenheim, in Upper Bavaria, where it occurs as a white, crystalline efflorescence on the stumps of fossil pine trees which project above the surface of the turf. The best solvents for fichtelite are light petroleum and chloroform, and from the former large, measurable crystals can readily be obtained. The vapour-density of the hydrocarbon is 7·6, and therefore Clark's formula, $C_{40}H_{70}$ (*Annalen*, **103**, 236), is inadmissible. Fichtelite is remarkably stable (compare Hell, this vol., p. 614), and it is very difficult to obtain derivatives from it; one compound, probably dehydrofichtelite, has, however, been prepared by heating it with iodine, whereby hydrogen iodide is evolved and a yellow syrup obtained. This distils at 290—295° under a pressure of 270 mm. as a thick and almost colourless oil, showing a beautiful bluish-violet fluorescence. W. P. W.

A New Dihydroxynaphthalene. By A. CLAUS (*J. pr. Chem.* [2], **39**, 315—317).—When naphthalene-α-hydrazinesulphonic acid is heated with dilute sulphuric acid, *β-naphthol-α-sulphonic acid* is obtained; its *barium* salt was analysed. When this new sulphonic acid is melted with potash, *β-α-dihydroxynaphthalene*, $C_{10}H_6(OH)_2$, is formed; it crystallises from hot water in white crystals melting at 134—135° (uncorr.), and is soluble in most solvents; from benzene it crystallises in short prisms. It becomes red on exposure to the air, and gives a blue fluorescence in alkaline solution, but not in alcoholic solution; some other reactions are given. The *acetyl*-derivative, $C_{10}H_6(OAc)_2$, is at first obtained as an oil, but solidifies after a time; it crystallises in beautiful, colourless prisms, melting at 73° (uncorr.).

By heating β-naphthol-α-sulphonic acid with phosphorus pentachloride, a chloronaphthol melting at 128°, and a dichloronaphthalene melting at 48—49° (compare Abstr., 1887, 963), were obtained. A. G. B.

Thionaphthols. By F. KRAFFT and R. SCHÖNHERR (*Ber.*, **22**, 821—826).—The authors find that the thiophenol or dihydroxyphenyl sulphide obtained by Krafft by boiling diazothiobenzene, prepared from thioaniline, with water (*Ber.*, 7, 384, 1164) is identical with Tassinari's hydroxyphenyl sulphide (Abstr., 1887, 807).

α-Thionaphthol, $C_{10}H_7\cdot SH$, is obtained by treating sodium α-naphthalenesulphonate (20 parts) with phosphorus pentachloride (18·5 parts), slowly adding the whole product to a cooled mixture of zinc-dust (40 parts) and dilute sulphuric acid (1 : 3) (240 parts), and afterwards heating for one to two hours in a reflux apparatus. It is a colourless, heavy, strongly refractive oil with a faint odour of mercaptan, boils at 152·5—153·5° under a pressure of 15 mm., and at 286° under the ordinary atmospheric pressure, and has a sp. gr. of 1·1729 at 0°, 1·1549 at 23°, and 1·0971 at 98·8° (compared with water at 4°). The *ethyl*-derivative, $C_{10}H_7\cdot SEt$, is an oil boiling at 167—167·5° under a pressure of 15 mm., and has a sp. gr. of 1·1198 at 0°, 1·0797 at 50°, and 1·0419 at 98·8°. The *acetyl*-derivative, $C_{10}H_7\cdot SAc$, boils at 188° under a pressure of 15 mm., and has a sp. gr. of 1·1519 at 50·1° and 1·1138 at 98·8°. The *benzoyl*-derivative, $C_{10}H_7\cdot SBz$, melts at 116—117°, and boils at 262° under a pressure of 15 mm. α-Naphthyl sulphide (Armstrong, this Journal, 1875, 803), obtained by distilling the lead salt of α-thionaphthol, crystallises from alcohol in slender, concentrically-grouped needles, melts at 110°, and boils at 289—290° under a pressure of 15 mm.

β-Thionaphthol, prepared in like manner from sodium β-naphthalenesulphonate, melts at 81°, and boils at 153·5° under a pressure of 15 mm., and at 286° under the ordinary pressure, and is readily soluble in alcohol and ether, but sparingly soluble in water. The *ethyl*-derivative melts at 16°, and boils at 170·5° under a pressure of 15 mm.; the acetyl-derivative melts at 53·5°, and boils at 191° under a pressure of 15 mm.; the *benzoyl*-derivative melts at 108°, and boils without decomposition at 267° under a pressure of 15 mm. β-naphthyl sulphide, obtained by distilling the lead salt of β-thionaphthol under a pressure of 10 mm., crystallises in thin scales, melts at 151°, boils at 295—296° under a pressure of 15 mm., and is sparingly soluble in hot alcohol, readily soluble in carbon bisulphide.

W. P. W.

α-Tetrahydronaphthylamine. By E. BAMBERGER and F. BORDT (*Ber.*, **22**, 625—634).—The following azo-colouring matters have been prepared from α-tetrahydronaphthylamine. *Phenylazo-α-tetrahydronaphthylamine*, $Ph\cdot N_2\cdot C_{10}H_{10}\cdot NH_2$, crystallises from alcohol in beautiful steel-blue needles showing a vitreous lustre, and is slightly soluble in water, benzene, and chloroform, but readily soluble in alcohol and ether forming dark Bordeaux-red solutions. *Sulphophenylazo-α-tetrahydronaphthylamine*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_{10}\cdot NH_2$, is sparingly soluble in cold but readily soluble in hot water and in alcohol, yielding dark orange-red solutions. The *sodium* salt crystallises from water in bright orange-red tables, showing a diamond lustre. *α-Tetrahydronaphthylazo-α-naphthylamine*, $C_{10}H_{11}\cdot N_2\cdot C_{10}H_6\cdot NH_2$, is obtained by diazotising α-tetrahydronaphthylamine and adding the diazo-compound to an acetic acid solution of α-naphthylamine. It crystallises from alcohol in tufts of slender, brick-red, silky needles, and melts at 135°. In this reaction a second compound is also formed which is less soluble in alcohol, crystallises in small green cubes, and dissolves in acetic acid with a violet colour. *α-Tetrahydronaphthylazoresorcinol*, $C_{10}H_{11}\cdot N_2\cdot C_6H_3(OH)_2$, crystallises from alcohol in slender, brick-red scales, and dissolves in alcohol, concentrated sulphuric acid, and alkalis with a dark, Bordeaux-red colour.

A comparison of the absorption-spectra of azo-dyes obtained from α-naphthylamine and α-naphthol, and from the tetrahydrogenated compounds, shows that in concentrated solutions strong absorption takes place in the blue and violet, and that in more dilute solutions the maximum absorption occurs between the green and blue. In the case of the colouring matters belonging to the normal series, absorption commences at some point between the yellow and green, whilst in that of colouring matters derived from the hydrogenated compounds, it commences at some point in the green or blue. In the table, the figures give the wave-lengths at which absorption commences.

α-Naphthylamine combined with	λ.	Tetrahydro-α-naphthylamine combined with	λ.
Diazobenzene chloride……	557·6	Diazobenzene chloride……	538·47
Sodium diazobenzenesulphonate……	569·84	Sodium diazobenzenesulphonate……	532·35
Diazobenzenesulphonic acid..	531·35	Diazobenzenesulphonic acid.	508·24
α-Naphthol combined with		Tetrahydro-α-naphthol combined with	
Diazobenzene chloride……	534·65	Diazobenzene chloride……	492·93
Sodium diazobenzenesulphonate……	562·19	Sodium diazobenzenesulphonate……	505·58

α-Tetrahydronaphthonitrile, $C_{10}H_{11}\cdot CN$, prepared by Sandmeyer's method from tetrahydro-α-naphthylamine hydrochloride, is a colourless, viscid liquid, having a slight nitrile-like odour and boiling at 277—279° under a pressure of 721 mm. Tetrahydro-α-naphthol is also formed in the preparation of the nitrile, and constitutes about one-third of the product. When the nitrile, dissolved in alcoholic ammonia, is treated with hydrogen sulphide and allowed to remain for some days at 30—40°, *α-tetrahydronaphthothiamide*, $C_{10}H_{11}\cdot CS\cdot NH_2$, is obtained; it is a dark yellow oil. Digestion with alcoholic potash at 160—170° for five to six hours converts the nitrile into a mixture of amide and acid; *α-tetrahydronaphthamide*, $C_{10}H_{11}\cdot CONH_2$, crystallises in flat, satiny needles, melts at 182°, and is sparingly soluble in cold water; *α-tetrahydronaphthoic acid*, $C_{10}H_{11}\cdot COOH$, crystallises in slender prisms, melts at 128°, and is sparingly soluble in cold alcohol and in hot water.

When α-tetrahydronaphthylamine is diazotised, and the diazo-compound reduced with stannous chloride, *α-tetrahydronaphthylhydrazine hydrochloride*, $C_{10}H_{11}\cdot NH\cdot NH_2,HCl$, is obtained in silvery scales. The base crystallises from light petroleum in white prisms which aggregate in the form of long needles, is sparingly soluble in water, readily soluble in alcohol, ether, benzene, and hot petroleum, and reduces Fehling's solution at a temperature of 30—40°. When suspended in boiling water and treated with copper sulphate solution, it is converted into *α-tetrahydronaphthalene*, $C_{10}H_{12}$, which is a colourless oil, having a strong odour of naphthalene and boiling at 206° under a pressure of 708 mm. W. P. W.

Relation between the Chemical Properties and Constitution of Hydrogenated Bases. By E. BAMBERGER (*Ber.*, **22**, 767—778).—In order to distinguish the two classes of hydrogenated bases derived from α- and β-naphthylamine, the author proposes that those containing both the amidogen and the added hydrogen atoms in the same nucleus shall be termed "alicyclic" (ἄλειφαρ and *cyclus*), and those containing amidogen in the one and the four added hydrogen atoms in the second nucleus shall be termed "aromatic" tetrahydro-bases. A comparison, based on the researches of the author in conjunction with Müller (Abstr., 1888, 599, 712), Althausse (Abstr., 1888, 959), Bordt (preceding Abstract), and Baumann (*Ber.*, **22**, 963), is instituted between the properties of the two classes of tetrahydro-bases.
W. P. W.

1 : 1′-Naphthylenediamine. By O. HINSBERG (*Ber.*, **22**, 861).—1 : 1′-Naphthylenediamine is known to resemble orthodiamines in forming condensation compounds with various reagents. The author finds, however, that it does not form an azine on treatment with phenanthraquinone and thus differs from the true orthodiamines.
W. P. W.

Hydronaphthalic Acid. By F. ANSELM (*Ber.*, **22**, 859—860).—On reduction with sodium amalgam, naphthalic acid is converted into *dihydronaphthalic acid*, $C_{10}H_8(COOH)_2$, and a second reduction product. Dihydronaphthalic acid is crystalline, decomposes at 199° with the evolution of carbonic anhydride and water, and is readily soluble in warm alcohol, sparingly soluble in ether, benzene, and water.
W. P. W.

α-Naphtholsulphonic Acids. By F. BENDER (*Ber.*, **22**, 993—1000).—The methods hitherto described for the purpose of characterising the various α-naphtholsulphonic acids (estimation of the water of crystallisation of salts, &c.), are untrustworthy, since they fail to sharply distinguish one acid from another. It is possible, however, to identify each of the known α-naphtholsulphonic acids by its behaviour with diazo-compounds and nitrous and nitric acids, and the author describes the reactions of each with these reagents. No methods of separating the various acids from the product obtained on sulphonating α-naphthol are given, and it would seem that the acids examined were technical products prepared in the ordinary way by the methods given in the various patents to which reference is made.

The following α-naphtholsulphonic acids have been prepared:—

(1.) α-Naphtholsulphonic acid (Schaeffer, *Annalen*, **152**, 293; Baum, German Specification B 4197 of June 30, 1883).

(2) α-Naphthol-α-sulphonic acid [OH : SO_3H = 1 : 4] obtained from naphthionic acid (Neville and Winther, Trans., 1880, 632; Actiengesellschaft für Anilinfabrikation, German Patent 46307); these acids are characterised by forming azo-dyes, by yielding dinitro-α-naphthol on treatment with nitric acid (the nitration being attended with the formation of resinous substances and the production of a red coloration), and by forming well-crystallised nitroso-compounds, which, on nitration, are readily converted into dinitro-α-naphthol.

(3.) α-Naphtholsulphonic acid (Liebmann, German Specification L 4327). This acid forms azo- and disazo-dyes, gives a small yield of dinitro-α-naphtholsulphonic acid on nitration, red vapours being evolved, and forms a well-crystallised nitroso-derivative, which is converted by nitration into dinitro-α-naphtholsulphonic acid.

(4.) α-Naphtholdisulphonic acid employed technically for the production of dinitro-α-naphthol. This acid yields neither azo-dyes nor nitroso-derivatives.

(5.) α-Naphtholdisulphonic acid (Leonhardt and Co., English Patent 11318, of August 18, 1887, &c.). This acid yields azo-dyes and nitroso-compounds, and on nitration behaves like Liebmann's acid, forming dinitro-α-naphtholsulphonic acid.

(6.) α-Naphtholtrisulphonic acid (Badische Anilin- und Sodafabrik, German Patent 10785). This acid forms neither azo-dyes nor nitroso-compounds, and on nitration is readily converted into dinitro-α-naphtholsulphonic acid.

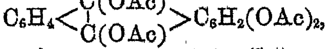
The action of sulphuric acid on α-naphthol is complicated by the fact that certain of the sulphonic acids readily undergo partial hydrolysis in the presence of the hot and relatively dilute sulphuric acid formed in the process of sulphonation, whilst others of the acids are stable under the same conditions. An examination of the sulphonation product of α-naphthol seems to show that with fuming sulphuric acid, Schaeffer's and Neville and Winther's acids very rapidly undergo further sulphonation, forming, first, the disulphonic acid No. 4, and then the trisulphonic acid which by partial hydrolysis is converted into the disulphonic acid No. 5; with ordinary sulphuric acid, a small quantity only of trisulphonic acid is formed, the disulphonic acid No. 4 being converted into the isomeric No. 5 acid. W. P. W.

Constitution of β-Naphthylamine-α-sulphonic Acid. By S. FORSLING (*Ber.*, **22**, 619—620).—The bromonaphthalenesulphonic acid obtained by Sandmeyer's method from β-naphthylamine-α-sulphonic acid can be converted into a dibromonaphthalene which melts at 75°, and is identical with that described by Meldola (Trans., 1885, 497). Meldola has assigned the constitution 1 : 2′ or 1 : 3′ to this dibromonaphthalene. The dichloronaphthalene obtained from β-naphthylamine-α-sulphonic acid melts at 62° (Abstr., 1887, 962), and, inasmuch as Erdmann and Kirchhoff have assigned the constitution 1 : 2′ to a dichloronaphthalene melting at 61·5° (this vol., p. 150), it follows in the author's opinion that β-naphthylamine-α-sulphonic acid has the constitution [$SO_3H : NH_2 = 1 : 2'$]. (Compare Armstrong and Wynne, Proc., 1889, 50). W. P. W.

Hydroxysulphonaphthoic Acids. By K. König (*Ber.*, **22**, 787—789).—*α-Hydroxysulphonaphthoic acid*, $OH·C_{10}H_5(COOH)·SO_3H + 5H_2O$, is prepared by adding α-hydroxynaphthoic acid (1 part) to a well-cooled mixture of sulphuric acid containing 20 per cent. of sulphuric anhydride (2 parts), and concentrated sulphuric acid (3 parts), and afterwards heating the solution at 60°. It crystallises in small shimmering needles, and is readily soluble in water and alcohol. The *sodium hydrogen* salt, $C_{11}H_7O_6SNa$, crystallises in slender, silky needles; the *basic sodium* salt, $C_{11}H_5O_6SNa_3$, crystallises in long needles, which rapidly effloresce on exposure to the air; the *barium hydrogen* salt, $(C_{11}H_7O_6S)_2Ba$, and normal *barium* salt, were also prepared.

α-Hydroxydisulphonaphthoic acid, $OH·C_{10}H_4(COOH)(SO_3H)_2 + 4H_2O$, is obtained by sulphonating α-hydroxynaphthoic acid with four times its weight of fuming sulphuric acid. It crystallises in stellate groups of white needles, and is very soluble in alcohol and water. The *potassium hydrogen* salt, $C_{11}H_6O_9S_2K_2$, and normal *barium* salt, $(C_{11}H_5O_9S_2)_2Ba_3$, are described. W. P. W.

Hystazarin Compounds. By A. Schoeller (*Ber.*, **22**, 683—685; compare Abstr., 1888, 1203).—*Barium hystazarin*, $C_{14}H_6O_4Ba$, is formed when an alcoholic solution of hystazarin is treated with a few drops of ammonia diluted with water, and precipitated with baryta-water. It is quickly filtered, and the dark blue salt dried, first over sulphuric acid, and then at 130°. The *calcium compound* is a dark violet precipitate. The *diethyl ether*, $C_{14}H_6O_2(OEt)_2$, is obtained together with the mon-ethyl compound, when equal parts of potash and hystazarin are treated with a little water, and boiled with ethyl iodide (5 parts) for three hours. The excess of ethyl iodide is distilled off and the residue filtered. The precipitate, which is the diethyl compound, crystallises from alcohol in light yellow needles melting at 160—163°. The *monethyl ether*, $OEtC_{14}H_6O_2·OH$, is precipitated from the alkaline solution by acid, and crystallised from alcohol. It forms yellow needles, which melt at 234—240°, and dissolves in alkalis and in ammonia, yielding carmine-red solutions.

Hystazarin tetracetyloxanthranol,  $C_6H_4{<}\begin{matrix}C(OAc)\\|\\C(OAc)\end{matrix}{>}C_6H_2(OAc)_2$, is prepared by boiling hystazarin (1 part), sodium acetate (1·5 part), acetic anhydride (12 parts), and zinc-dust (3 parts), for three hours. It crystallises from alcohol in long, colourless crystals melting at 217—219°. When the acetyl groups are removed by Liebermann's method, a reduction-compound of hystazarin, $C_{28}H_{18}O_6$, is formed. This dissolves in alkalis with green colour. N. H. M.

Perhydrides of the Higher Aromatic Hydrocarbons. By C. Liebermann and L. Spiegel (*Ber.*, **22**, 779—781; compare this vol.,

p. 405).—*Phenanthrene perhydride*, $C_{14}H_{24}$, is obtained, together with a small quantity of a compound poorer in hydrogen, when phenanthrene (1 part) is heated at about 250° for 12 to 16 hours with amorphous phosphorus ($1\frac{1}{4}$ parts), and hydriodic acid of sp. gr. 1·7 (5—6 parts). It melts at −3°, and its sp. gr. at 20° is 0·933. It is not acted on by nitric acid, bromine, or fuming sulphuric acid in the cold, and it is only slightly attacked by a boiling glacial acetic acid solution of chromic acid. When distilled over zinc-dust, it is to a great extent decomposed, yielding only small quantities of phenanthrene, but also relatively larger quantities of anthracene.

Retene dodecahydride, $C_{18}H_{30}$, prepared in like manner, is a colourless oil with a bluish fluorescence, boils at 336° (uncorr.), and is sparingly soluble in cold glacial acetic acid. It yields small quantities of retene when distilled over zinc-dust, and when treated with bromine in carbon bisulphide solution, hydrogen bromide is rapidly evolved. It is only slowly acted on by cold, fuming nitric acid, but it is readily attacked when boiled with chromic acid in glacial acetic acid solution.

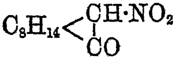
Picene perhydride, $C_{22}H_{36}$, is obtained, together with smaller quantities of *picene icosihydride*, $C_{22}H_{34}$ (an oil boiling about 360°), when picene is reduced with hydriodic acid, as described above. It crystallises from alcohol in colourless needles, melts at 175°, boils above 360°, and in behaviour resembles retene and phenanthrene perhydrides. It yields picine when distilled over zinc-dust.

Acenaphthene perhydride, $C_{12}H_{20}$, is a colourless liquid boiling at 235—236° (uncorr.).

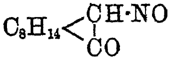
Fluorene perhydride, $C_{13}H_{22}$, is a colourless liquid boiling at 230° (uncorr.).

The authors think it probable that many of these hydrides may occur, not only in coal-tar, but also in the tar obtained from lignite. (Compare Liebermann, Abstr., 1878, 861.) F. S. K.

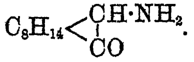
Reduction of Nitro-camphor to Nitroso-camphor. By P. CAZENEUVE (*Compt. rend.*, **108**, 857—859).—300 grams of chloronitro-camphor and 1500 grams of alcohol of 93° were boiled for about half an hour with a zinc-copper couple made by the action of a solution of 100 grams of cupric sulphate on 600 grams of granulated zinc. The liquid was filtered, the filtrate distilled to dryness, the cupric oxychloride removed by treatment with warm dilute hydrochloric acid, and the residue recrystallised from alcohol. The nitroso-camphor thus obtained is a white, crystalline solid, insoluble in water, and only slightly soluble in cold alcohol, but more soluble in boiling alcohol or benzene. It alters when exposed to light, becomes greenish, and gives off nitrogen oxides. It is neutral to litmus and orange III, but acid to phenolphthaleïn. The rotatory power as determined with a 3·81 per cent. solution in benzene is $[\alpha]_D = +195°$. Nitro-camphor is strongly lævogyrate. Nitroso-camphor does not melt before decomposing; at 180° it suddenly becomes green, intumesces, and evolves nitrogen oxides. If thrown on red hot platinum, it detonates. It dissolves in alkalis, but seems to alter when the solutions are boiled, and if fused with potassium hydroxide at 150° it yields potassium nitrite and carbonate. It has no action on ferric chloride. Fuming nitric acid, or a mixture of nitric and sulphuric acids, convert it almost quantitatively into equal molecular proportions of camphoric acid and camphoric anhydride. Tin and hydrochloric acid reduce nitroso-camphor to an amido-derivative identical with that obtained by the reduction of nitro-camphor. The three compounds seem to have the constitution—



$$C_8H_{14}<\begin{array}{l}CH{\cdot}NO_2\\ \mid\\ CO\end{array}$$



$$C_8H_{14}<\begin{array}{l}CH{\cdot}NO\\ \mid\\ CO\end{array}$$



$$C_8H_{14}<\begin{array}{l}CH{\cdot}NH_2\\ \mid\\ CO\end{array}.$$

The reduction of a nitro-derivative to a nitroso-derivative in this manner is unusual. Reduction does not take place if absolute alcohol is used. The water present yields hydrogen, and the chlorine in the chloronitro-camphor is first removed in the form of cuprous chloride, which then changes into cupric chloride, and finally forms cupric oxychloride. C. H. B.

The Camphor Series. By E. BECKMANN (*Annalen*, **250**, 322—376).—*Menthone*, discovered by Moriya (Trans., 1881, 77) and investigated by Atkinson and Yoshida (Trans., 1882, 50), is a mixture of two isomerides, one of which is dextrogyrate and the other lævogyrate. The *lævomenthone*, $C_{10}H_{18}O$, is prepared by actively shaking together 45 grams of crystallised menthol with a solution of 60 grams of potassium dichromate in 300 grams of water and 50 grams of strong sulphuric acid. The temperature of the solution at the beginning of the operation should be about 30°. The temperature generally rises to 55° in about half an hour, and then falls. If the temperature does not reach this point, the mixture is carefully warmed; if, on the other hand, the temperature rises rapidly, the mixture is cooled down to 55°. The menthone is extracted from the crude product with ether, the extract is washed with water and with dilute alkalis until colourless. It is then rapidly distilled in small quantities at a time in a current of steam and dried over anhydrous sodium sulphate. Lævomenthone is a colourless liquid with a bitter taste and an odour of peppermint. It is sparingly soluble in water, but mixes readily with other solvents. It boils at 207°, and its sp. gr. at 20° is 0·896. The molecular weight as determined by Raoult's method, using benzene as the solvent, corresponds with the formula $C_{10}H_{18}O$. The molecular refraction for the sodium line is 46·41. The oxime is prepared by adding sodium hydrogen carbonate to an alcoholic solution of menthone and hydroxylamine hydrochloride. The mixture is warmed for some minutes, and on the addition of water, the oxime separates as an oily liquid which soon crystallises. It is purified by recrystallisation from dilute alcohol, ether, or light petroleum; it melts at 58°. Raoult's method of determining the molecular weight by the depression of the freezing point of acetic acid gives results agreeing with the formula $C_{10}H_{18}NOH$ when dilute solutions are used, but the molecular weight increases with the concentration of the solution. If benzene is used, values ranging from 251 to 292 are obtained. The oxime dissolves readily in dilute acids, but ether extracts the oxime from these acid solutions.

The *hydrochloride*, $C_{10}H_{18}NOH,HCl$, prepared by passing dry hydrogen chloride into an ethereal solution of menthoneoxime, crystallises from absolute alcohol in plates, and is decomposed by water; it melts at 118—119°. A sodium compound is formed when solid sodium ethoxide is added to an ethereal solution of lævogyrate menthoneoxime.

Dextromenthone is prepared by freezing a mixture of 10 parts of strong sulphuric acid and 1 part of water: 2 parts of menthone are added to the frozen acid, and the mixture is actively shaken. The temperature is slowly raised to 30°, and the product is poured on to a large quantity of ice. The dextromenthone is extracted with ether and purified in the same way as lævomenthone. It closely resembles its isomeride in its properties; it boils at 208°, and its sp. gr. compared with water at 20° is 0·9. The *oxime* is liquid. The determination of its molecular weight by Raoult's method gives similar results to those obtained with the lævo-oxime. The hydrochloride melts at 95—100°, and deliquesces on exposure to the air. The sodium compound resembles the corresponding isomeric sodium-derivative.

Dilute sulphuric, hydrochloric, or acetic acids convert both lævo- and dextro-menthone into a mixture of lævo- and dextro-menthones, which turns the ray of polarised light to the right. Alkalis and even water yield similar results. The rotatory power of the menthones slowly changes at the ordinary temperature; the change takes place more rapidly at a high temperature.

Dextrocamphor is not inverted by the action of heat, acids, and alkalis like the menthones. The oxime and its hydrochloride are both lævogyrate. Lævocamphor is not inverted by treatment with strong sulphuric acid. The oxime and its hydrochloride turn the ray of polarised light to the right. Determinations of the molecular weight of the two isomeric camphors give results agreeing with the formula $C_{10}H_{16}O$. The oximes are deposited from a mixture of ether and light petroleum in monoclinic crystals; the crystals are hemimorphous. In the oxime of dextrogyrate camphor, the clinodome predominates on the left side of the crystal, and in the oxime of the lævogyrate camphor it predominates on the right. Menthol and menthoneoxime are not inverted by dilute acids or alkalis. The following table exhibits the specific and molecular rotation of the compounds:—

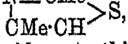
Compounds.	Specific rotation.	Molec. rotation.	Oxime.		Oxime hydrochloride.	
			Sp. rotation.	Molec. rotation.	Sp. rotation.	Molec. rotation.
Lævogyrate menthol....	−49·35	−76·99	—	—	—	—
Lævogyrate menthone ..	−28·18	−43·40	−41·97	−70·93	−61·16	−125·7
Dextrogyrate menthone .	+28·14	+43·34	−4·85	−8·20	−24·48	−50·31
Lævogyrate borneol	−37·74	−58·12	—	—	—	—
Dextrogyrate borneol ...	+37·74	+57·66	—	—	—	—
Lævocamphor	−44·22	−67·21	+42·51	+70·99	+42·52	+86·53
Dextrocamphor	+44·22	+67·21	−42·40	−70·81	−43·98	−89·50

Menthol is a derivative of benzene hexahydride of the constitution [Pr : Me : OH = 1 : 4 : 5], menthone being regarded as its ketone.

The paper concludes with a discussion of the geometrical constitution of these compounds. W. C. W.

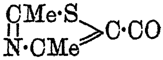
Gymnemic Acid. By D. Hooper (*Chem. News*, **59**, 159—160).—*Gymnemic acid* occurs in combination in the leaves of *Gymnema sylvestre*, *G. hirsuta*, and *G. montanum*, and is precipitated by mineral acids from the aqueous solution of the alcoholic extract of the leaves. The dry acid, $C_{32}H_{55}O_{12}$, melts at 60°, decomposes above 100°, is a brittle, black resin, greenish when in powder, soluble in alcohol, ether, benzene, and chloroform, slightly so in amyl alcohol and carbon bisulphide, insoluble in water. With potash, soda, or ammonia, it forms a red solution from which it is reprecipitated by acids. It is also dissolved by concentrated sulphuric or nitric acid with a red colour, and in both mixtures it is destroyed and precipitated by water; but by prolonged contact with nitric acid, it forms a soluble nitro-compound. It is precipitated by lead acetate, silver nitrate, ferric chloride, and by barium and calcium salts, but not by tannin, picric acid, or gelatin. It forms insoluble salts with alkaloïds. It is a glucoside, and although neither it nor its salts have been obtained in crystals, analyses of the acid and the lead and silver salts, also the alkali saturating coefficient, indicate that it has the above composition and is monobasic. D. A. L.

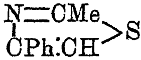
Thiazoles from Thiamides. By A. Hantzsch (*Annalen*, **250**, 257—273).—The thiazoles closely resemble the pyridine-bases in their physical properties, for instance, in boiling point, odour, and solubility. They are mobile liquids with a neutral reaction to litmus; their salts have an acid reaction. The mono- and di-alkylthiazoles are formed by the action of thiamides on α-chloraldehydes or α-chloroketones. The thiamides of the fatty acids are most conveniently prepared by a modification of Hofmann's method: for example, thiacetamide is prepared by warming for a few minutes an intimate mixture of acetamide (5 mols.) and phosphorus pentasulphide (1 mol.) with several times the volume of benzene.

α-μ-Dimethylthiazole,  $\begin{matrix}N\equiv CMe\\ | \\ CMe\cdot CH\end{matrix}\!>\!S$, is prepared by the action of chloracetone on thiacetamide. As this action is very energetic, it is advisable to add alcohol or water to moderate its violence. Most of the properties of this substance have already been enumerated by the author (Abstr., 1888, 574). The liquid boils at 144—145·5° (corr.), and its sp. gr. at 15° is 1·0601. The *platinochloride* forms thick prisms soluble in water; it melts with decomposition at 215°. The *picrate* melts at 137—138°, but dimethylpyridine picrate melts at 159—161°. The double salt, $C_5H_7NS,HCl,4HgCl_2 + 4H_2O$, is precipitated when an excess of mercuric chloride is added to a strong solution of dimethylthiazole hydrochloride. The salt melts at 110°, and is freely soluble in water. Dimethylthiazole produces in a solution of mercuric chloride a precipitate of the composition

$$C_5H_7SN,2HgCl_2.$$

This compound is sparingly soluble in cold water, but dissolves freely in dilute hydrochloric acid. It melts with decomposition at 176—177°. The *methiodide*, C_5H_7SN,MeI, is soluble in water, and forms fine crystals. It decomposes about 225°.

Ethyl dimethylthiazolecarboxylate, 
$\begin{array}{l}\text{CMe·S}\\ \|\\ \text{N·CMe}\end{array}\!>\!\text{C·COOEt}$ (Abstr., 1888, 574), crystallises in needles, melts at 50—51°, and boils at 242—242·5° (corr.). It is soluble in alcohol and ether, and unites with mineral acids to form salts. It is not decomposed by boiling with hydrochloric acid and potassium chlorate.

μ-Methyl-α-phenylthiazole, 
$\begin{array}{l}\text{N}{\equiv}\text{CMe}\\ |\\ \text{CPh:CH}\end{array}\!>\!\text{S}$, melts at 68·5°, and boils at 284° (corr.). The hydrochloride and hydrobromide are partially decomposed by water, in which they are sparingly soluble.

μ-Methylthiazole (*loc. cit.*) is prepared by adding thiacetamide to crude monochloraldehyde obtained by the action of anhydrous oxalic acid on monochloracetal at 140°. The base is miscible with water; it boils at 127·5—128° (corr.). The hydrochloride and hydrobromide form deliquescent needles. The *picrate* forms yellow needles, soluble in alcohol and benzene; it melts at 145—146°. The *platinochloride* forms six-sided plates and flat needles, and is freely soluble in water; it melts at 199° with decomposition. The mercurochloride crystallises in rhombic prisms melting at 111—112°. The double compound of the base with mercuric chloride melts at 154·5°. The monomethyl base differs from dimethylthiazole in giving no precipitate with silver nitrate, and by being completely oxidised by a mixture of hydrochloric acid and potassium chlorate. W. C. W.

Thiazoles from Amidothiazoles. By G. Popp (*Annalen*, **250**, 273—280).—Amidothiazoles are converted into thiazoles by acting on them with nitrous acid and decomposing the product by boiling alcohol.

A good yield of thiazole is obtained by gradually adding an alcoholic solution (20 per cent.) of ethyl nitrite to 10 grams of amidothiazole hydrochloride dissolved in 300 grams of (98 per cent.) boiling alcohol. The product is evaporated with water, filtered, rendered alkaline by the addition of potash or potassium carbonate, and distilled; solid potassium hydroxide is added to the distillate until the thiazole separates out; it is then dried over potassium hydroxide and distilled. Thiazole is a colourless, mobile, highly refractive liquid. It is hygroscopic, and boils at 116·8°. Its sp. gr. at 17° is 1·1998 compared with water at the same temperature. The hydrochloride forms small, deliquescent crystals. The platinochloride, $(C_3H_3SN)_2,H_2PtCl_6 + 2H_2O$, crystallises in prisms soluble in alcohol and in hot water. It melts at 110° and decomposes at 250°. The aurochloride,

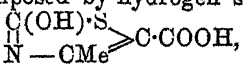
$$C_3H_3SN,HAuCl_4,$$

crystallises from alcohol in small prisms; this salt melts with decomposition at 248—250°. The picrate melts at 151°, and is deposited from hot water in silky needles. The mercurochloride, $C_3H_3SN,HHgCl_3$, forms silky needles, and melts at 103—104°. The compound $C_3H_3SN,HgCl_2$ melts at 202—204°.

α-Methylthiazole has been described by Arapides (Abstr., 1888, 573). The aurochloride melts at 184—185° with decomposition. A large excess of a concentrated solution of mercuric chloride produces with α-methylthiazole, in the presence of hydrochloric acid, a crystalline precipitate of the mercurochloride melting at 119°. In the absence of hydrochloric acid a double compound is formed, which melts at 148°. α-Phenylthiazole, also described by Arapides (this vol., p. 414), melts at 52°, and boils at 273°. The salts crystallise well, but are decomposed by water. The hydrochloride melts at 80°. The platinochloride, $(C_9H_7NS)_2,H_2PtCl_6 + 2H_2O$, forms long needles and melts at 196°. The aurochloride is deposited from alcohol in small needles, almost insoluble in water; it melts with decomposition at 174—175°. The picrate melts at 164—165°, and the mercurochloride at 152—153°. W. C. W.

Action of Thiocyanates and Thiocarbamide on Chlorinated Ethyl Acetoacetate. By H. ZÜRCHER (*Annalen*, **250**, 281—294).—Ethyl hydroxymethylthiazolecarboxylate has been described by Hantzsch and Weber (Abstr., 1888, 258). On the addition of an aqueous solution of hydroxylamine to an alcoholic solution of the ethereal salt, *methylthiazolehydroxamic oxide*,

$$O(C_3NSMe\cdot CO\cdot NH\cdot OH)_2,$$

is formed, and is obtained after evaporating the alcohol in transparent, prismatic crystals, sparingly soluble in water, ether, and benzene. This compound melts about 215—220° with decomposition. Ethyl hydroxymethylthiazolecarboxylate forms potassium and sodium salts, which are sparingly soluble in cold water, but dissolve more freely in warm alcohol and in warm water. In order to obtain the free acid, the ethereal salt is dissolved in an excess of an alcoholic solution of potassium hydroxide; after two days the alcohol is removed by evaporation, the residue dissolved in water, neutralised with nitric acid, and the acid precipitated by silver nitrate. The silver salt is suspended in water and decomposed by hydrogen sulphide. *Methylhydroxythiazolecarboxylic acid*,  $\begin{array}{l}C(OH)\cdot S \\ \| \\ N - CMe\end{array}\!\!>\!C\cdot COOH$, melts at 100° in its water of crystallisation. The anhydrous acid does not melt at 200°, but blackens. The acid is freely soluble in water and alcohol. The *ammonium salt*, $C_5NSH_4O_3\cdot NH_4 + 5H_2O$, crystallises in needles, and is freely soluble in water. The salt has a neutral reaction.

The hydrochloride of *ethyl amidomethylthiazolecarboxylate*,

$$COOEt\cdot C_3NSMe\cdot NH_3Cl,$$

is formed by the action of ethyl monochloracetoacetate on thiocarbamide. It crystallises in prisms. Sodium hydroxide throws down a crystalline precipitate of the ethereal salt from solutions of the hydrochloride. Ethyl amidomethylthiazolecarboxylate melts at 175° and dissolves freely in mineral acids and alcohol. The nitrate and platinochloride are crystalline. A solution of the ethereal salt in an alcoholic solution of potassium hydroxide soon deposits crystals of potassium amidomethylthiazolecarboxylate. The free acid is liberated by the action of dilute acetic acid on the potassium salt. It is a white, crystalline powder, which decomposes without melting. It dissolves in acids and in alkalis, but is insoluble in most neutral solvents. The *hydrochloride* crystallises in plates. The *platinochloride*,

$$3C_5H_6N_2O_2S,2H_2PtCl_6,$$

is crystalline. The potassium salt forms precipitates in solutions of silver, mercury, zinc, lead, tin, cadmium, and ferric salts.

Ethyl dichloracetoacetate acts on barium thiocyanate, forming a small quantity of a crystalline compound, $C_{14}H_{16}O_7N_2S_2$, melting at 160—165°.

Ethyl dichloracetoacetate has no action on thiocarbamide.

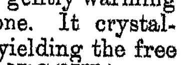
W. C. W.

Selenocyanogen- and Selenazole-compounds.

By G. HOFMANN (*Annalen*, **250**, 294—322).—*Selenocyanacetone*, COMe·CH$_2$·SeCN, is obtained in an impure state by acting on monochloracetone with potassium selenocyanate.

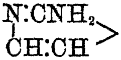
Ethyl selenocyanacetoacetate, COMe·CH(SeCN)·COOEt, is prepared by the action of ethyl monochloracetoacetate on potassium selenocyanate. *Selenocyanacetophenone*, COPh·CH$_2$·SeCN, formed by boiling an alcoholic solution of monobromacetophenone and potassium selenocyanate, is crystalline, and melts at 85°. This substance has a great tendency to form resins. All attempts to convert the selenocyanoketones into the isomeric hydroxyselenazoles failed. *Selenocyanacetic acid*, COOH·CH$_2$·SeCN, is prepared by warming a concentrated solution of potassium monochloracetate with solid potassium selenocyanate. The potassium salt crystallises in plates soluble in water. The acid crystallises in yellow needles and melts at 84—85°; it is freely soluble in water, alcohol, and ether, and decomposes carbonates. The salts are not characteristic. The SeCN radicle is not capable of taking up water to form the group SeCONH$_2$, and in this way give rise to selenazole-derivatives.

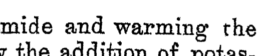
α-Methylselenazylamine hydrochloride is formed on gently warming a mixture of selenocarbamide and monochloracetone. It crystallises in long prisms, and is decomposed by alkalis, yielding the free base. *α-Methylselenazylamine* (*amidomethylselenazole*),

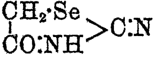


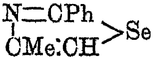
$\begin{matrix}N\!:\!C(NH_2)\\ |\qquad\\ CMe\!:\!CH\end{matrix}\!\!>\!Se$,

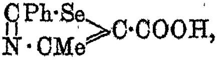
crystallises in needles, and melts at 79—80°. It is soluble in alcohol, ether, and benzene, and has a strongly alkaline reaction. Its salts crystallise well, but blacken on exposure to the light. The *platinochloride*, $(C_4H_6N_2Se)_2,H_2PtCl_6$, is sparingly soluble. The *acetyl* derivative, C$_3$NSeHMe·NHAc, is sparingly soluble, and melts at 122°. *α-Phenylselenazylamine*, prepared from selenocarbamide and bromacetophenone crystallises in needles, and melts at 132°. The hydrobromide crystallises in plates which are freely soluble in hot water.

Selenazylamine,  $\genfrac{}{}{0pt}{}{\text{N:CNH}_2}{\text{CH:CH}}>\text{Se}$, is prepared by adding dichlorether to a solution of sodium acetate and selenocarbamide and warming the mixture; the product is rendered alkaline by the addition of potassium carbonate and the azylamine extracted with ether. The base melts at 121°, and dissolves in benzene, alcohol, and water. The platinochloride and the acetyl derivative are crystalline. The latter melts at 210° with decomposition.

α-Methylselenazylamine-β-carboxylic acid hydrochloride is formed when ethyl chloracetoacetate acts on selenocarbamide. It is a crystalline powder, soluble in water. The free acid,  $\genfrac{}{}{0pt}{}{\text{N——CMe}}{\text{C(NH}_2\text{)·Se}}>\text{C·COOH}$, crystallises in needles, and melts at 195°. It is freely soluble in alcohol and ether, and in caustic alkalis. It cannot decompose carbonates. The acetyl derivative melts at 220° with decomposition.

Selenhydantoïn,  $\genfrac{}{}{0pt}{}{\text{CH}_2\text{·Se}}{\text{CO:NH}}>\text{C:NH}$, is prepared by boiling an alcoholic solution of monochloracetic acid and selenocarbamide. It is soluble in hot water, turns litmus blue, and forms crystalline salts. It is decomposed by boiling with water, yielding *α-μ-dihydroxyselenazole*. This crystallises in long prisms, melts at 147°, and is soluble in alcohol and water. In water it easily forms supersaturated solutions. Attempts to obtain selenacetamide in appreciable quantities were unsuccessful.

In the presence of alcohol, selenbenzamide interacts with chloracetone, forming *μ-phenyl-α-methylselenazole*,  $\genfrac{}{}{0pt}{}{\text{N}{=}\text{CPh}}{\text{CMe:CH}}>\text{Se}$; this is a liquid boiling at 282—283° under 736 mm. pressure, and is miscible with the usual solvents. The salts of this base are decomposed by water. *α-μ-Diphenylselenazole* is soluble in alcohol, ether, and benzene, and melts at 99°. The *platinochloride* is partially decomposed by water.

α-Methyl-μ-phenylselenazole-β-carboxylic acid,  $\genfrac{}{}{0pt}{}{\text{CPh·Se}}{\text{N·CMe}}>\text{C·COOH}$, is obtained in the form of an ethyl salt by the action of ethyl chloracetacetate on selenobenzamide. The free acid melts at 206—207°, but begins to sublime at 130°. It dissolves in alcohol and benzene. The acid forms a crystalline nitrate. The ethyl salt crystallises in plates and melts at 123—124°.

Attempts to prepare the free selenazoles from amide selenazoles were unsuccessful. W. C. W.

Direct Synthesis of Homologues of Pyrroline. By G. Ciamician and C. M. Zanetti (*Ber.*, **22**, 659—661).—When potassium pyrroline is boiled with ethyl iodide for four hours, treated with water and steam-distilled, an oil is obtained which consists chiefly of ethylpyrroline boiling at 130—134°; the fraction of higher boiling point (150—200°) is boiled with potash with which the greater part combines. On decomposing the product, an oil consisting of a mixture of isomeric ethylpyrrolines is obtained. The oil not acted on by potash contains *diethylpyrroline*, $C_8H_{13}N$, boiling at 165—175°.

N. H. M.

Action of Methyl Iodide on α-Methylpyrroline. By G. Ciamician and F. Anderlini (*Ber.*, **22**, 656—659).—*Trimethylpyrroline*, $C_7H_{11}N$, is prepared by heating methylpyrroline (3 grams), dissolved in methyl alcohol (5 grams) with methyl iodide (7 grams) and potassium carbonate (3 grams) for 10 hours at 140°. The product is acidified with dilute hydrochloric acid and steam-distilled. The aqueous distillate obtained after the methyl iodide and alcohol have passed over is extracted with ether, dried with soda, and distilled. It forms the chief product and boils between 150° and 165°.

The aqueous residue from the steam-distillation was treated with potash, again steam-distilled, and the bases so obtained evaporated down with hydrochloric acid and then heated with hydrochloric acid at 130°. The bases were then recovered in the usual manner, distilled under diminished pressure, dissolved in hydrochloric acid, and precipitated with gold chloride. The aurochloride, $C_{10}H_{17}N,HAuCl_4$ (this vol., p. 59), is obtained. The base, $C_{10}H_{17}N$, contains a methyl-group more than that obtained by the action of methyl iodide on sodium carbopyrrolate (*loc. cit.*). The base obtained from 1-methylpyrroline may therefore be considered as 1-methyldihydroparvoline or pentamethyldihydropyridine, $C_5NMeH_2Me_4$. N. H. M.

Formation of Pyridine from Amidoazonaphthalene. By K. Buchka and C. Sprague (*Ber.*, **22**, 826—829).—The authors find that when α-amidoazonaphthalene is reduced with stannous chloride and hydrochloric acid in alcoholic solution, pyridine is not formed as stated by Perkin (this Journal, 1863, 207). Friedländer (this vol., p. 607) arrived at the same conclusion. F. S. K.

γ-Bromoquinoline. By A. Claus and H. Decker (*J. pr. Chem.* [2], **39**, 301—314). — *Orthonitro-γ-bromoquinoline* crystallises in lustrous, colourless needles ($a : b : c = 0·7279 : 1 : 0·1432$) melting at 124° (uncorr.). It forms no methiodide. The *platinochloride* is described. 4 : 4′-*Nitrobromoquinoline* forms colourless, slender, soft and flexible, lustrous needles melting at 136—137°, and soluble in hot alcohol and other solvents. It has a peculiar smell and irritates the skin. Tin and hydrochloric acid colour it red; with mercuric chloride it gives a white precipitate which melts at 185°. The *platinochloride* is described. The *methiodide* crystallises in large, thin, lustrous, dark-red tablets, or in needles; it melts with decomposition at 205—210°, and is sparingly soluble. When digested with silver chloride, it is converted into the *methochloride* which crystallises in colourless needles, carbonising at 204°; the *platinochloride* of this last is described. The *ethiodide* is also described. These halogen alkyl compounds have an intensely bitter taste.

Ananitro-γ-bromomethylquinoline, $C_9NH_4MeBr·NO_2$ [$NO_2 : Me : Br = 4 : 1' : 4'$], is obtained by decomposing the above methiodide with the calculated quantity of ammonia at 0°; it forms yellow needles containing water; with alcohol (1 mol.) it crystallises in small, thick, monosymmetric tables ($a : b : c = 1·0964 : 1 : 1·1412$) melting with decomposition at 111°. The crystals formed with iso- and normal-propyl alcohol and with methyl alcohol are described.

4 : 4′-*Amidobromoquinoline*, formed by reducing the nitro-compound with stannous chloride, crystallises in lustrous, yellow needles, melting at 135° (uncorr.) and easily soluble. It dissolves in dilute acids with an intensely red colour, but its solution in concentrated acids is colourless, becoming red on the addition of water. The *acetyl*-derivative crystallises in white, lustrous needles melting at 212° (uncorr.), and dissolves in cold acids with a yellow colour which changes to red on heating or evaporating. The *diazochloride platinochloride* has been obtained.

4 : 4′-*Dibromoquinoline* is formed when the cold diazobromide solution (from a hydrobromic solution of the amidobromoquinoline and sodium nitrite) is added to a solution of cuprous bromide at 90° and then distilled with steam; it crystallises from alcohol in white, slender, pearly needles melting at 85—86° (uncorr.); they are very soluble and sublime. The *hydrochloride* and *platinochloride* are described. A. G. B.

Constitution of Lepidene. By G. Magnanini and A. Angeli (*Ber.*, **22**, 853—856).—When a warm acetic acid solution of oxylepidene is treated with a solution of phenylhydrazine acetate, a complicated compound is obtained which crystallises from alcohol in small, orange-red needles and melts at about 380° with decomposition. When oxylepidene is boiled with potash and an alcoholic solution of hydroxylamine hydrochloride, it yields a yellow, amorphous substance, readily soluble in alcohol and ether, but almost insoluble in light petroleum.

Hydro-oxylepidene is identical with bidesyl. (Compare Knoevenagel, Abstr., 1888, 706.)

Hydro-oxylepidene and both the bidesyls are readily converted into lepidene (m. p. 172—173°) when heated for two to three hours at 130—140° with concentrated hydrochloric acid.

These results show that in all probability lepidene is identical with tetraphenylfurfurane, a view which has already been put forward by Japp and Klingemann (*Ber.*, **21**, 2234), and that thiolepidene (thionessal) is probably tetraphenylthiophen. F. S. K.

Artificial and Natural Alkaloïds. By A. Colson (*Compt. rend.*, **108**, 677—679).—When commercial benzidene is submitted to Skraup's reaction, it yields the diethyl ether of a diquinolyl of oxyphenylene, $C_{22}H_{18}N_2O_3$, which has been previously described. It also yields a diquinolyl, $C_{18}H_{12}N_2$, which is not volatile in steam, and is only slightly soluble in water or in ether. It melts at 178°, and is identical with the diquinolyl described by O. Fischer and Weidel.

The *stannosochloride* of the first base, $C_{22}H_{18}N_2O_3,2SnCl_2$, forms lemon-yellow, prismatic needles, which melt at 135° and are almost insoluble in water. The *hydrochloride* is a yellow, crystalline salt, very soluble in water. The *hexabromide*, obtained by the action of excess of bromine-water, is a yellow, curdy substance insoluble in water and acids, but soluble in alcohol. It melts at 130° and decomposes with intumescence, leaving a carbonaceous residue. When treated with an alcoholic solution of hydrogen sulphide, it loses bromine.

When quinine is dissolved in dilute sulphuric acid and treated with bromine-water, it yields an abundant precipitate, the composition of which depends on the proportion of bromine added and the method of drying the product. All the products are yellow, curdy precipitates, only slightly soluble in water. They lose bromine readily, and decompose without melting at 160—180°. Only a small quantity of hydrobromic acid is formed simultaneously, and it follows that the precipitates are additive products.

Quinine tetrabromide is obtained by the action of 200 c.c. of 3 per cent. bromine-water on 5 grams of quinine. It is unstable, is readily altered by heat, has a bitter taste, and does not give the quinine reaction with chlorine-water and ammonia. If an alcoholic solution of the tetrabromide is treated with hydrogen sulphide and the product is evaporated on a water-bath, it yields a transparent, resinous residue, and if this is treated with a small quantity of warm water, the liquid deposits quinine tribromide on cooling. The aqueous solution is then mixed with ammonia, and quinine dibromide separates as a white precipitate containing 2 mols. H_2O. Both products yield platinochlorides.

C. H. B.

Acid Nicotine Tartrate. By H. DRESER (*Arch. Pharm.* [3], **27**, 266—270).—A hot concentrated alcoholic solution of tartaric acid is added to the free, undiluted liquid base, when the acid tartrate soon separates as a white syrup; after cooling, more alcoholic solution is added until opalescence only follows. After a time ether is repeatedly added, in not too great portions, as long as opalescence follows, to precipitate the tartrate retained in solution by the alcohol; the excess of tartaric acid remains dissolved if too great an excess of ether is not used. After remaining until clear, the ether is decanted and the residue is dissolved in a little boiling alcohol and filtered to remove a little resinous turbidity. On slowly cooling, a brown, amorphous, resinous impurity separates before the crystalline tartrate, whose complete separation is facilitated by the gradual addition of ether.

Acid nicotine tartrate, $C_{10}H_{14}N_2(C_4H_6O_6)_2 + 2H_2O$, forms white crystalline tufts, easily soluble in water, with an acid reaction. For analysis, the salt was precipitated with platinum chloride.

J. T.

Harmine and Harmaline. By O. FISCHER (*Ber.*, **22**, 637—645; compare Abstr., 1885, 820).—*Tetrahydroharmine*, $C_{13}H_{16}N_2O$, is obtained when harmine or harmaline is reduced with sodium and alcohol; it crystallises in spear-like needles, melts at 199°, and in solution shows a pale, bluish-green fluorescence. It is a secondary base, and forms a yellow *nitroso*-derivative, $C_{13}H_{15}N_3O_2$.

Harmine tetrabromide, $C_{13}H_{12}N_2OBr_4$, is formed by treating a solution of harmine in dilute sulphuric acid with excess of bromine-water in the cold. It is a reddish-yellow precipitate, and loses its bromine when treated with sulphurous acid or when warmed with alkaline carbonates or alcohol.

Harmalol, $C_{12}H_{12}N_2O + 3H_2O$ (*loc. cit.*), crystallises in beautiful red needles, and is soluble in hot water, chloroform, and acetone, but only sparingly soluble in benzene. The *hydrochloride*, $C_{12}H_{12}N_2O,HCl + 2H_2O$, and *platinochloride*, $(C_{12}H_{12}N_2O)_2,H_2PtCl_6$, were prepared. The *acetyl*-compound, $C_{14}H_{16}N_2O_3$, forms yellow crystals.

On oxidation with chromic acid, harmaline is converted into harminic acid, harmine being most probably formed as an intermediate product in the reaction, since it can be obtained by carefully oxidising harmaline with nitric acid. When harminic acid is heated in small quantities in a vacuum, it is converted into a well-crystallised base, *apoharmine*, $C_8H_8N_2$. This forms an *aurochloride*, $C_8H_8N_2,HAuCl_4$, crystallising in bright-yellow needles; a *hydriodide*, $C_8H_8N_2,HI + H_2O$, crystallising in white, fan-like groups of needles; and a *tetrabromide*, $C_8H_8N_2Br_4$. On reduction with hydriodic acid and amorphous phosphorus, it yields *dihydroapoharmine*, $C_8H_{10}N_2$, which crystallises in well-formed, lustrous tables, melts at 48—49°, boils at 262°, and is soluble in ether, but only sparingly soluble in light petroleum. The *hydrochloride*, $C_8H_{10}N_2,HCl$, crystallises from alcohol in slender, matted needles; the *platinochloride*, $C_8H_{10}N_2,H_2PtCl_6 + 2H_2O$, forms compact, prismatic, yellow crystals; the *aurochloride* $C_8H_{10}N_2,HAuCl_4$, crystallises in reddish-brown needles melting at 149° with decomposition; and the *nitrosamine*, $C_8H_9N_3O$, crystallises in small needles melting at 134—135°.

When fused with potassium hydroxide, harmol is converted into *harmolic acid*, $C_{12}H_{10}N_2O_5$, which crystallises in small needles, and melts at 246—247° with decomposition. On distillation, the acid yields a compound, $C_{11}H_{10}N_2O$, crystallising in white, spear-like forms; this dissolves readily in alkali, and also forms a *platinochloride*, $(C_{11}H_{10}N_2O)_2,H_2PtCl_6$, crystallising in stellate groups of prisms.

Ladenburg's methenyltoluylenediamine (this Journal, 1877, ii, 752) melts at 114°, and on treatment in methyl alcohol solution with methyl iodide yields the *hydriodide* of *methylmethenyltoluylenediamine*, $C_9H_{10}N_2,HI + H_2O$. The base obtained from the salt is an oil boiling at about 280°. Methenylphenylenediamine, in like manner, yields a methylated base, $C_8H_8N_2$, which crystallises in white prisms, melts at 33°, boils at 278° under 730 mm. pressure, and forms an *aurochloride*, $C_8H_8N_2,HAuCl_4$, crystallising in yellow needles. W. P. W.

Coca Bases. By O. HESSE (*Ber.*, 22, 665—671).—The crude bases from coca (Truxillo) were treated with light petroleum, which left a certain amount of cocamine undissolved; this was repeatedly dissolved in dilute acetic acid and precipitated with ammonia. Analyses of the pure base and of the hydrochloride point to the formulæ $C_{19}H_{23}NO_4 + \frac{1}{2}H_2O$ and $C_{19}H_{23}NO_4,HCl + H_2O$, but the water of crystallisation could not be determined exactly, as both the free base and the salt decompose when heated. When the hydrochloride is heated at 120°, it is converted into cocamylecgonine, $C_{18}H_{21}NO_4$, and methyl chloride; a small quantity of cocaïc acid is also formed. A similar reaction takes place when an aqueous solution of the hydrochloride is boiled in presence of hydrochloric acid; the cocamylecgonine formed is decomposed into ecgonine and cocaïc acid.

Cocaïc acid, $C_9H_8O_2$, purified by boiling the crude substance with calcium hydroxide, precipitating with hydrochloric acid, and crystallising from glacial acetic acid, forms small, colourless plates melting at 266°. It dissolves sparingly in ether, rather readily in hot alcohol. The *lead salt*, $(C_9H_7O_2)_2Pb + H_2O$, crystallises in small needles. The acid is identical with Liebermann's γ-isatropic acid (Abstr., 1888, 1211). Ecgonine hydrochloride melts with effervescence at 234—238° (not 246°, Liebermann, *loc. cit.*).

Cocamine acts on the organism similarly to cocaïne, but the action is more feeble; its anæsthetic action is especially weak, and it seems to have no poisonous properties.

Cocrylecgonine is obtained by treating the residue from the light petroleum extract of crude coca bases with sulphuric acid and potassium permanganate and subsequent fractional precipitation. The product is dissolved in ether, and the residue, obtained by evaporating off the ether, kept for some time at 60°. It is then treated with acid, the undissolved portion dissolved in dilute ammonia, and precipitated with dilute acid; it is purified by redissolving in ammonia and fractional precipitation with hydrochloric acid, and is obtained as a yellowish-white powder melting at 120°. When boiled with dilute hydrochloric acid for a long time, it is converted into ecgonine and *cocrylic acid*, $C_{18}H_{19}NO_4$. Cocrylecgonine is also obtained by boiling so-called isatropylcocaïne with hydrochloric acid, and is probably formed from cocrylamine mixed with isatropylcocaïne. The poisonous properties ascribed by Liebermann to isatropylcocaïne are probably due to the presence of cocrylamine.

The solution from which crude cocamine was precipitated yielded an oil which was boiled with hydrochloric acid; ecgonine, hygrine, which has the formula $C_{12}H_{13}N$, cocaïc acid, much cinnamic and some benzoic acid, were obtained. N. H. M.

Coca Bases. By C. LIEBERMANN (*Ber.*, **22**, 672—675).—A reply to Hesse (preceding Abstract). The low melting point (266°) ascribed by Hesse to γ-isatropic acid (cocaïc acid), which melts at 274°, was probably due to the substance having been insufficiently purified. With regard to the poisonous properties of isatropylcocaïne which Hesse believes to be due to the presence of impurities (*loc. cit.*), the author maintains that his isatropylcocaïne was pure.

N. H. M.

Hygrine. By C. LIEBERMANN (*Ber.*, **22**, 675—679).—The hygrine was prepared from coca-leaves by Lossen's method (*Annalen*, **133**, 352). The crude product was dissolved in absolute ether, dried with potash, and distilled under 45—50 mm. pressure. Two fractions were obtained, the one (one third of the whole) boiling at 128—131°, and the other at about 215°. Before the last distillation, a current of dry air or nitrogen is passed through the substance heated at 120°, or it is dried with potash at the same temperature.

The base of lower boiling point has the formula $C_8H_{15}NO$. It boils at 193—195° (corr.) at the ordinary pressure. Sp. gr. = 0·940 at 19° compared with water at the same temperature. The *picrate* crystallises in yellow needles, melts at 148°, and is rather soluble in cold water. The base is quite different from tropine, which has the same composition, and can only be identical with Calmels and Gossin's isotropine (Abstr., 1885, 912) if this was a very impure substance, which, it is suggested, is probable.

The base of higher boiling point, $C_{14}H_{24}N_2O$, does not distil without decomposition at the ordinary pressure. Sp. gr. at 18° = 0·982 compared with water at 18°. The *hydrochloride*, $C_{14}H_{24}N_2O,2HCl$, the *aurochloride*, $C_{14}H_{24}N_2O,2HAuCl_4$, which forms yellow flakes, the *picrate* and the *methiodide* were analysed. It is probable that the substance contains a small amount of a lower homologue, $C_{13}H_{22}N_2O$.

N. H. M.

δ- and γ-Isatropylcocaïne. By C. Liebermann and W. Drory (*Ber.*, **22**, 680—683).—δ-Isatropylecgonine, $C_9H_7O{\cdot}C_9H_{14}NO_3$, is prepared by heating finely-powdered ecgonine (1 part) with isatropic anhydride (one part) and benzene (two parts) in a reflux apparatus on a water-bath for one or two hours; the product is washed with benzene, dried, powdered, and extracted with water. The residue consists of δ-isatropic acid and δ-isatropylecgonine; these are separated from each other by means of boiling alcohol, which dissolves the acid very readily. Isatropylecgonine crystallises in colourless needles, melts at 202° with decomposition, is insoluble in water, ether, and benzene, readily soluble in ammonia and acids. When boiled with mineral acids, it is decomposed into its components. The *aurochloride*, $(C_{18}H_{21}NO_4)_2,HAuCl_4$, and picrate form amorphous precipitates.

δ-Isatropylcocaïne, $C_9H_7O{\cdot}C_9H_{13}MeNO_3$, prepared from the above compound by methylation, resembles in all respects the natural base.

γ-Isatropyl chloride, C_9H_7OCl, is obtained by heating γ-isatropic acid with phosphoric chloride (1 mol.) for half an hour in a water-bath, distilling off the phosphorus oxychloride, and crystallising the residue from a mixture of benzene and light petroleum. It crystallises (with $\frac{1}{2}$ mol. C_6H_6) in clear prisms, which rapidly lose benzene on exposure to air, and melt at 125°.

γ-Isatropic anhydride, $(C_9H_7O)_2O$, prepared by boiling sodium γ-isatropate with γ-isatropyl chloride, forms a chalk-like powder.

γ-Isatropylecgonine is prepared in a manner similar to the δ-compound. It was not obtained pure, but was converted into the cocaïne compound by passing hydrogen chloride through the solution in methyl alcohol. γ-Isatropylcocaïne is identical with the natural base; it has a bitter taste, and when treated with mineral acids yields the pure γ-acid melting at 274°.

ε-Isatropyl chloride is prepared similarly to the δ-compound; it crystallises from a mixture of benzene and light petroleum in long, silky needles melting at 140°.

N. H. M.

Ptomaïnes. By O. de Coninck (*Compt. rend.*, **108**, 809—810).—The potassium salt of the pyridinecarboxylic acid obtained by oxidation of the alkaloid $C_{18}H_{11}N$ (this vol., p. 58), was converted into the cupric salt, which was then suspended in alcohol and decomposed by hydrogen sulphide. The alcoholic filtrate was concentrated, and the acid which crystallised was converted again into the potassium salt, and the same process repeated. The final alcoholic solution was mixed with hydrochloric acid, and evaporated in a vacuum, when crystals of the hydrochloride of nicotinic acid, $C_5NH_4{\cdot}COOH + HCl$, were obtained.

This result confirms the previous conclusion that the alkaloïd $C_8H_{11}N$ and nicotine yield the same pyridinecarboxylic acid on oxidation.
C. H. B.

Physiological Chemistry.

Artificial versus Animal Digestion. By E. F. Ladd (*Amer. Chem. J.*, **11**, 162—172).—By means of the artificial digestion of food-stuffs, the relative digestibility for the proteïds of the several substances can be determined, and the coefficients obtained serve as a measure of the digestibility of the fodder. These figures, moreover, are approximately equal to those obtained in actual digestion with animals. The results in round numbers for four different kinds of food were as follows:—

	Artificial digestion.	Animal digestion.
Corn fodder........	54	49
Soja hispida........	75	70
Orchard grass hay ..	62	60
Corn meal	64	58

Other experiments were performed with similar results, and from the data obtained the following conclusions are drawn:—

1. That pepsin furnishes us with a trustworthy means of determining the digestibility of the albuminous material of foods, and that this serves as a good criterion of the digestibility of the fodder itself.
2. That the coefficients of digestibility for proteïds as usually calculated from animal digestion are too low.
3. That the digestibility of the proteïds of corn meal, as given in the German tables, seems to be too high for ruminants.
4. That in many feeding-stuffs the proteïd matter is all present in a digestible form.
5. That the digestion of the fæces by a pepsin solution probably gives results above what is actually digested by the animal.

W. D. H.

Free Hydrochloric Acid in Gastric Juice. By Boas (*J. Pharm.* [5], **19**, 238—239, from *Pharm. Zeit. Russland*, **28**, 1889, 10, through *Pharm. Zeit.*, 1888, 752).—A test solution is prepared by dissolving 5 grams of resorcinol and 3 grams of cane-sugar in 100 grams of dilute alcohol. Two or three drops of this reagent is added to 5—6 drops of gastric juice, and the mixture is heated in a porcelain capsule over a very small flame. After complete evaporation, the sides of the capsule are coated with a rose or bright-red varnish in the presence of free hydrochloric acid. The colour changes gradually on cooling. Too strong a heat carbonises the sugar, and the reaction is masked. The coloration is produced when not more hydrochloric acid than 0·05 : 1000 is present. The test can also be applied on a strip of filter-paper. Albuminoïd substances interfere with this test in the same way that they interfere with Günsburg's (phloroglucinol-vanilline) test, in such a manner that they may partially or completely neutralise the hydrochloric acid present in the gastric juice.

J. T.

Assimilation of Milk-sugar. By BOURQUELOT and TROISIER (*J. Pharm.* [5], **19**, 277—282).—Milk-sugar is not directly assimilated. Dastre has shown that when injected into the veins of a dog, it is all found unchanged in the urine. To serve for nutrition, the lactose then must undergo a digestive transformation; nothing positive is known of this transformation and mode of assimilation. A diabetic patient on a milk diet was treated with increasing quantities of lactose, and the sugar voided in the urine was estimated as glucose both by the polarimeter and by Fehling's solution. The two methods gave concordant results, proving the absence of galactose. The sugar was also separated from the urine, crystallised, and found to be glucose. The amount obtained increased with the amount administered, and equalled, or almost equalled, that amount, showing that the lactose is finally converted into glucose. The experiments do not, however, show how the transformation is effected. J. T.

Digestibility of Soiling Rye. By W. FREAR (*Bied. Centr.*, 1889, 229—231).—The green rye employed had the composition—Water, 84·33 per cent.; fat, 0·77; fibre, 4·72; cellulose, &c., 6·35; albuminoïds, 2·50; ash, 1·33. Of the total nitrogen 50·48 was present as non-albuminoïds.

The following are the coefficients of digestion (ox) obtained:—

Total dry matter, 73·6; fat, 74·2; fibre, 79·6; cellulose, 70·6; albumin, 79·1: ash, 55·5. E. W. P.

Amount of Glycerol in the Residuary Liquors of Brandy Distillation. By H. v. TÖRRING (*Landw. Versuchs-Stat.*, **36**, 29—60).—The object of the investigation was to determine the amount of glycerol in various residuary liquors of brandy distillation, as well as the relation which the amount of glycerol bears to the nutritive value of the liquor.

The following method was employed for estimating the glycerol:—The filtrate from the liquor (30 c.c.) is evaporated down to about 5 c.c., mixed with burnt gypsum (15 grams), and the whole well ground up. The powder is extracted with absolute alcohol for six hours, and the solution, to which water (10 to 20 c.c.) is added, distilled under diminished pressure. The distilling apparatus consists of a small retort (about 100 c.c. capacity) and a short condenser, the lower end of which is bent down so as to pass into a strong flask, which is connected with a water-pump. The retort is heated in an air-bath, first at 150—170°, until the whole of the water has distilled over; the apparatus is then connected with a water-pump, and the temperature of the air-bath raised to 190—210°. To remove the last traces of glycerol from the retort and condenser, a few c.c. of water are put into the retort and distilled over at the ordinary pressure. The glycerol in the distillate is determined as benzoate by Diez's method (Abstr., 1887, 750). If the filtrate from the liquor is distilled and the glycerol determined in the distillate, low results are obtained, probably owing to the retention of a portion of the glycerol in the voluminous residue in the retort.

Glycerol was determined in seven samples of these residues from different sources; the mean percentage of glycerol in dry substance is 3·12, which corresponds with 252 grams per hectolitre of liquor. Theoretically, 1 hectolitre of liquor should yield 354 to 521 grams of glycerol. The fact that a less amount of glycerol was found than that required by theory is probably due to the partial fermentation of the glycerol, which might also account for the presence of propyl and butyl alcohols in crude spirit.

A sample of the dried residue of commerce was found to contain only 1·9 per cent. of glycerol in the dry substance. It is shown that about half of the glycerol may be lost in the drying.

A comparison is made of the nutritive value of glycerol and that of the other food constituents of the liquors (compare Arnschink, Abstr., 1887, 509). According to Maercker, the greatest amount of potato-spirit liquor given to a fattened ox is 120 litres, which would contain, at most, 360 grams of glycerol, or 0·6 gram per kilo. of live-weight (with an ox weighing 600 kilos.), an amount too small to act injuriously. The average amount (75 litres) of liquor given to an ox contains: proteïds 1455 grams, fat 105 grams, non-nitrogenous extract 2821 grams (containing glycerol 225 grams), crude fibre 937 grams, and ash 690 grams. The non-nitrogenous nutritive substances of the liquor are starch, unfermented maltose, and dextrin. The more rational the management, the smaller is the amount of these substances present in the liquor, and the more important the glycerol. From this standpoint, glycerol is a more important nutritive constituent of liquor than it would seem, considering the relatively small amount of it which is present. N. H. M.

Chemical Composition of Cartilage. By C. T. Mörner (*Skand. Arch. f. physiol.*, 1, 210—243).—In a previous article (Abstr., 1888, 860) the microchemical reactions of hyaline cartilage were stated to indicate the existence of two materials in the matrix, a collagenous network, and spherical masses filling up the meshes, which were termed chondrin balls. The present article deals more especially with the macrochemical investigation of the same material, the tracheal cartilage.

The following four substances were found in the matrix:—

(1.) Chondro-mucoid: a substance very like mucin, but differing from it in not being stringy. It contains 12·58 per cent. of nitrogen, 47·3 of carbon, 6·42 of hydrogen, 2·42 of sulphur (of which 0·7 appears to be combined in the form of an ethereal hydrogen sulphate), and 31·28 of oxygen. The low percentage of nitrogen is very like that found in mucin.

On treatment with alkalis, it yields proteïd material (an albuminate and a peptone-like substance) and chondroitic acid. On treatment with acids, there is, in addition, free sulphuric acid.

(2.) Chondroitic acid. This appears to exist free in the matrix, and is not merely derived from the chondro-mucoid. It is a substance originally described by Krukenberg as a hyalin (Abstr., 1886, 481). In the present research, no substance corresponding to Krukenberg's hypothetical precursor or hyalogen was found.

This substance yields, on treatment with dilute mineral acids, a reducing sugar. The average results of elementary analyses gave, nitrogen 3·15 per cent., carbon 35·28, hydrogen 4·68, sulphur 6·33. The low percentage of nitrogen and high percentage of sulphur (all of which is present in the form of ethereal sulphate) is especially noteworthy.

(3.) Collagen, which, as usual, yields gelatin on boiling.

(4.) Albumoïd. A very insoluble form of proteïd. This is absent in young cartilage. The chondro-mucoid and chondroitic acid appear to be contained in the chondrin balls, the collagen and albumoïd in the network. W. D. H.

Relations between the Physiological Properties and Constitution of Hydrogenised Bases. By E. BAMBERGER and W. FILEHNE (*Ber.*, **22**, 777—778).—Bamberger (*Ber.*, **21**, 1124) has described the midriatic action of *ac.* β-tetrahydronaphthylamine, and Stein (*Virchow's Archiv*, **115**, 14) has shown that in the rabbit it produces the other well-known group of symptoms caused by excitation of the cervical sympathetic nerve (contraction of vessels of ear, ptosis, &c.). This appears to be due both to a central and peripheral action.

It is now found that the same drug raises the body temperature; this appears to be due to diminished loss, as well as increased production of heat.

Extending the investigation to the group of hydrogenised naphtha-

Midriatic.	Non-midriatic.
ac. β-Tetrahydronaphthylamine.	*ac.* α-Tetrahydronaphthylamine.
ac. β-Tetrahydroethylnaphthylamine.	*ar.* β-Tetrahydroethylnaphthylamine.
ac. β-Tetrahydrodimethylnaphthylamine.	*ar.* β-Tetrahydrodimethylnaphthylamine.
	ac. Tetrahydroamidonaphthol [1 : 4′].
	ac. Tetrahydronaphthylendiamine [1 : 4′].
	ar. Tetrahydronaphthylendiamine [1 : 2].
	ar. Tetrahydronaphthylendiamine [1 : 2].

lene bases, it was found that the alicyclic hydrogenised bases of the β-series were active; whereas other members of the group were not: the test for activity was the action on the pupil.

For explanation of the nomenclature, see this vol., p. 717.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Gases on the Development of Micro-organisms. By P. F. FRANKLAND (*Proc. Roy. Soc.*, **45**, 292—301).—Plate cultivations by the ordinary methods of *Bacillus pyocyaneus*, Koch's comma *spirillum* and Finkler's comma *spirillum*, were submitted under a bell-jar to hydrogen, carbonic oxide, carbonic anhydride, and nitrous oxide, the jar being sealed with mercury and sterilised water. Hydrogen was found to have the least, and carbonic anhydride the most deleterious effect on the organisms, hence, in anaërobic cultivations, hydrogen is the most suitable medium for expulsion of air, since even where bacteria give rise to carbonic anhydride, they may not reach their full activity unless the carbonic anhydride is removed. Boussingault (*Compt. rend.*, **91**, 37) has shown this to be the case for yeast. With regard to particular bacteria, the growth of *B. pyocyaneus* was arrested by carbonic anhydride, but recommenced on exposure to air, as observed by Fränkel; the growth of Koch's comma *spirillum* and Finkler's *spirillum*, was also arrested, and was not resumed on exposure to air. It was found that the power of resistance of individual organisms varied greatly. Experiments were also made with nitric oxide, hydrogen sulphide, and sulphurous anhydride, with the result that the organisms were destroyed. H. K. T.

Disengagement of Free Nitrogen during Putrefaction. By B. TACKE (*Ann. Agronom.*, **15**, 185—187).—The author has enclosed the putrefiable substances in flasks with drawn-out necks plunged in a mercury trough; the substances were introduced by a lateral tubulure, through which the air contained in the flask was afterwards removed by a pump, the flask being several times refilled with a gas free from nitrogen, and finally the tubulure was sealed with the blowpipe. In this way, percolation of atmospheric nitrogen into the apparatus was entirely avoided. The substances experimented on were flour, meat, clover, grass, sugar-beet, and various mixtures; the putrefaction was started by introducing small quantities of soil, mud, sewage, ripe cheese, &c. When nitrates are absent, free nitrogen was not produced in any appreciable quantity, whether in the absence or presence of oxygen. The gaseous products of putrefaction were carbonic anhydride, hydrogen, hydrogen sulphide, and marsh-gas. In presence of nitrates, and especially in absence of free oxygen, there was an energetic reduction with evolution of free nitrogen and all the lower oxides of nitrogen. J. M. H. M.

Putrefaction; Formation of Manures. By J. REISET (*Compt. rend.*, **108**, 708—710, and 779—785).—The author gives a summary of the results of experiments made by himself in 1856 (*Compt. rend.*, **52**), and by Lawes, Gilbert, and Pugh in 1860 (*Proc. Roy. Soc.*). One of the chief points established was the fact that in putrefactive fermentation a notable quantity of nitrogen is evolved in the gaseous state. Since that time, however, the importance of microbes in changes of this character has been recognized, and the author has therefore made a new series of experiments with various forms of nitrogenous organic matter. During the course of the experiment, oxygen was admitted regularly, by means of a special apparatus (*Ann. Chem. Phys.* [3], **26**, 299), into the vessel containing the fermenting substance.

In the case of horse dung mixed with chalk and water, the free nitrogen evolved was equal in volume to 0·546 per cent. of the oxygen consumed, 91·80 of the oxygen being converted into carbonic anhydride, and the remainder into other compounds. No combustible gas was evolved. With raw beef, also mixed with chalk and water, the nitrogen evolved was 2·177 per cent. of the oxygen consumed, 98·81 of the latter being converted into carbonic anhydride. No combustible gas was formed. In another experiment with beef, the evolved nitrogen was 5·95 per cent. of the volume of the oxygen.

In some of the earlier experiments, in which the ammonia was completely absorbed, it was found that the gas produced by the fermentation of manures in contact with water contained several per cents of methane. In anaërobic fermentation, the evolution of nitrogen is much greater than in the case of slow combustion in oxygen.

C. H. B.

Effect of Carbonic Oxide on Germination. By G. LINOSSIER (*Compt. rend.*, **108**, 820—822).—The author has previously shown that carbonic oxide has little effect upon the germination of seeds, and although when it amounts to 50 per cent. of the gas it retards germination to a considerable extent, it does not arrest it altogether even when it amounts to 75 per cent. Since Claude Bernard stated that a comparatively small quantity of the gas was sufficient to prevent germination, the author has made further experiments, mainly with a view to ascertain whether the effect observed was due to carbonic anhydride or some other cause. Experiments were made with seeds of cress and lettuce, the proportion of oxygen in the surrounding atmosphere being always 21 per cent., whilst the proportion of carbonic anhydride varied from 0 to 36 per cent. This gas causes a notable retardation when it amounts to 10 per cent., but does not prevent germination even when the proportion present is very high. The retardation was greater with the cress than with the lettuce. In order to ascertain whether a decrease in the pressure of the oxygen had any influence, air was mixed with carbonic anhydride so that the proportion of oxygen diminished. A somewhat longer time was required for germination than when the oxygen was kept constant, but germination was not prevented. Similar results were obtained by mixing air with imperfectly washed carbonic oxide. In no case was germination prevented, although the time required was in several cases increased by several hours, and the only supposition which seems capable of explaining Bernard's results is that he stopped his experiments at some point between the time required for germination in the air and the much longer time required in presence of carbonic oxide, &c.

C. H. B.

Reserve Materials of Trees. By R. HARTIG (*Ann. Agronom.* **15**, 190—191).—The author considers that the starch stored up in the living tissues of the wood in the autumn is not dissolved out during the next summer except as regards the contents of the one or two most recent annual rings, a very small quantity of reserve material sufficing to start the young shoots into growth until they are able to assimilate for themselves. The bulk of the reserve is regarded by the author as stored up in view of the flowering and fructifying season, when it is rapidly and completely exhausted. Some beech trees having fructified abundantly in 1888, the author found that from half to two-thirds of the reserve of starch had disappeared from the wood; not only so, but the wood was almost completely exhausted of nitrogen, containing in most places less than 0·01 per cent., whereas in 1886 the wood contained from 0·098 to 0·392 per cent., according to the position from which the samples were taken.

J. M. H. M.

Saccharine Substances in Fungi. By E. BOURQUELOT (*Compt. rend.*, **108**, 568—570).—The experiments were made with eight species of *Lactarius* and with *Boletus aurantiacus*. The young and fresh fungi were dried by exposure to air, then at 50—60°, and were extracted with boiling alcohol of 80°. The alcohol was distilled off and the liquid concentrated to a semi-syrupy consistency. After remaining under a desiccator for some time, the liquid deposited a quantity of crystals which when recrystallised from alcohol were found to be identical with mannitol. In no case was a sugar obtained which had any action on polarised light. The percentages of mannitol obtained from the various species were as follows:—*L. vellerius* (1886), 7·77; *L. vellerius* (1888), 2·14; *L. turpis*, 9·50; *L. piperatus*, 1·90; *L. pyrogalus*, 15·00; *L. controversus*, 4·90; *L. torminosus*, 5·10; *L. subdulcis*, 6·66; *L. pallidus*, 10·50. The amount varies considerably even in the same species, the variations being probably due to atmospheric conditions.

Fresh *L. piperatus* extracted with boiling water gave about 0·4 per cent. of trehalose, and a similar result was obtained with *B. aurantiacus*; the fresh fungus giving 0·7 per cent. of trehalose free from mannitol, whilst the dried fungus gave 7 per cent. of mannitol and no trehalose. The disappearance of the trehalose is doubtless due to a process of ripening. It is well known that the vegetation of fungi is very active, and the results described show that the vital processes continue during drying.

C. H. B.

Gluten in Wheat. By E. GATELLIER and L. L'HÔTE (*Compt. rend.*, **108**, 859—862).—In order to determine the influence of previous crops on the quality of wheat as measured by the amount of gluten which it contains, wheat was grown on three plots of a sandy soil, one of which had grown a crop of sugar-beet, the second a crop of oats preceded by lucerne, and the third a crop of "minette," followed by the application of 30,000 kilos. of manure per hectare. The nitrogen in the flour from the wheat was estimated by means of soda-lime, and the numbers were multiplied by Dumas and Cahours' coefficient, 6·25, in order to obtain the amount of gluten.

	After sugar-beet.	After oats and lucerne.	After "minette" and manure.
Nitrogen....	1·45	1·61	1·68
Gluten	9·06	10·06	10·50

The wheat containing the lowest proportion of nitrogen had the best appearance.

By manuring with ammonium sulphate and superphosphate, it was found possible to raise the percentage of nitrogen to 2·04, which corresponds to 12·75 per cent. of gluten. The best results were obtained with 300 kilos. of ammonium sulphate and 300 kilos. of superphosphate per hectare, the ratio of nitrogen to phosphoric anhydride being 12 : 9.

Experiments showed that the richness of the flour in nitrogen is in direct relation to the richness of the original wheat. In the latter case, the numbers are about 0·4 per cent. higher in consequence of the large quantity of nitrogen present in the envelope. The nitrogen in the grain is not all present as gluten, but if the total nitrogen is multiplied by the gluten coefficient, the numbers obtained are proportional to the quantity of gluten actually present. Analyses of the whole grain yield more accurate results than analyses of the flour, in consequence of the difficulty of obtaining a proper average sample of the latter.
C. H. B.

Constituents of Lycopodium Spores. By A. LANGER (*Arch. Pharm.* [3], **27**, 241—265, and 289—309).—In an exhaustive examination of these spores (from *Lycopodium clavatum*), the author finds (1) that they contain 1·155 per cent. of mineral constituents having a neutral reaction, and composed mainly of potassium, sodium, calcium, magnesium, iron, and aluminium phosphates, together with small quantities of calcium sulphate, potassium chloride, aluminium silicate, and traces of manganese. (2.) They contain 49·34 per cent. of a greenish-yellow oil with an acid reaction. This oil contains 80—86·67 per cent. of a fluid, fatty acid, variable amounts of glycerol, and a mixture of fixed fatty acids. The liquid acid, $C_{16}H_{30}O_2$, gives a lead salt soluble in ether; it belongs to the oleic acid series, and may be represented as *α-decyl-β-isopropylacrylic acid.* The fixed fatty acid appears to consist mainly of myristic acid. (3.) The spores yield monomethylamine when warmed or boiled with potassium hydroxide solution of 1·32 sp. gr. (4.) The dry commercial spores yield 0·857 per cent. of nitrogen. (5.) The spores contain at least 2·12 per cent. of saccharose. This is oxidised to acetaldehyde when the spores are macerated with alcohol; this action is due to the fact that oxygen is condensed to ozone by the spores. (6.) Fused with potassium hydroxide, the spores yield (*a*) a brown, resin-like, nitrogen-free compound of acid reaction and fæcal odour; (*b*) a non-nitrogenous benzene-derivative, forming needle-shaped crystals, soluble in ether and water, but not in chloroform, closely related to protocatechuic acid.

J. T.

Chemistry of Flax Fibre. By C. F. Cross and E. J. Bevan (*Chem. News*, **59**, 135—136).—The authors point out that ordinary flax is not pure bast, but that, in spite of retting and scutching, it retains a small proportion of residues of the wood ("sprit") and some cortical tissues; these impurities are, moreover, of considerable technical importance.

With regard to the pure fibre substance, Kolb showed that it is a compound of cellulose with a pectosic group, the constitution of which group the authors are now investigating. By the action of nitric acid, sp. gr. 1·15, on flax, they obtained a small amount of mucic acid, formed evidently from the non-cellulose flax constituents, some oxalic acid and carbonic anhydride, and fatty and wax acids, derived from the cuticular substances, and separable by means of alcohol from the fibrous residue of oxycellulose. By treatment with alkaline permanganate, pure flax cellulose yielded 45 per cent. of oxycellulose, 18 per cent. of oxalic acid, and 15 per cent. of a soluble carbohydrate of the aldehyde-alcohol type, yielding furfuraldehyde when hydrolysed by acids. The "sprit" is apparently a ligno-cellulose.

The *cuticular substances* are of much interest. Hot alcohol dissolves from scutched fibre 2 or 3 per cent. of a mixture consisting of—(1) a wax which is deposited on cooling; (2) a soluble carbohydrate of the ligno-cellulose type; (3) a green, semi-fused residue left after the extraction of (2) with boiling water, and resolved by benzene into a brown wax and a bright green oil; the latter becomes semi-solid on cooling when deprived of the solvent.

Wax (1) apparently consists of a free wax-alcohol and a compound of the same with a ketone-resin. The alcohol, $C_{23}H_{47}·OH$, melts at 81—82°, and yields an acetate, $C_{23}H_{47}·AcO$, melting at 65°. The resin, as also the brown wax and green oil, yield on further treatment indifferent, oily products, which are being examined. In general properties, the brown wax resembles wax (1), but the alcohol obtained by its saponification melts at 74°.

D. A. L.

Failure of Oat Crops. By P. Sorauer (*Bied. Centr.*, 1889, 266—272).—It frequently occurs that a crop of oats fails to mature without any apparent reason. The water culture of plants shows that oats are unable to mature if the solution by which they are surrounded is very strong; consequently it is recommended that when a crop of oats fails, and the evidence points to heavy manuring as the cause, then a drawing crop should be put on previous to the sowing with oats, so as to reduce to some extent the over-richness of the ground. It would also appear that as the nutrient solutions become more and more concentrated, a lesser amount of water is required for the production of dry matter, and this is accompanied by a more rapid growth and greater production. In poor soil, the roots distribute themselves over a greater extent, and take up more water than they otherwise would, so as to obtain the requisite amount of mineral matter. The deduction from these experiments is, that when there is a likelihood of a paucity of water, heavy manuring will make up for the want of water, as a lesser root growth is then necessary.

E. W. P.

Maize as Dry Food and as Silage. By E. H. JENKINS and others (*Bied. Centr.*, 1889, 231—237).—The analysis of various portions of maize plants indicates a great difference in their digestibility. There appears to be no difference in the digestibility of maize meal and the plant itself when given whole, and ensilage of the plant has no special effect on the yield of milk.

W. A. Henry fed cows with ordinary dry maize straw and with maize ensilage, both chopped fine. There appeared to be no difference in the yield of milk and butter under either condition. A similar result was obtained when the maize was not cut fine.

F. A. Woll finds an increase of specific gravity, but a decrease in the percentage of dry matter and caseïn when maize silage is used, and the digestibility of silage was higher than that of dried maize stems. Henry also finds that the loss in dry matter, whether by making maize into silage or hay, is practically the same, namely 20—25 per cent., and that cattle should have equal quantities of dry matter as silage or as hay; maize hay amounting to twice the weight of the silage must be given.

Tables are given by Woll and Short to show the changes in composition undergone by maize in silo as compared with the ripe maize itself, and it appears that the changes occurring in green maize are no greater than any other fodder plants experience. E. W. P.

Manuring of Barley. By J. HANAMAN (*Bied. Centr.*, 1889, 223—225).—After 20 years of experimenting, the author has come to the conclusion that small plots of, say, 10 square metres do not give accurate results, yet he holds with experiments in pots, as these give results consistent with one another.

He has now made experiments in iron cylinders 260 mm. high and 140 mm. broad, on the growth of barley manured with phosphates, nitrogen, and potash. As the soil employed was rich in potash, potash manures produced no increase, whilst phosphates greatly increased the yield of grain but not of straw; nitrogen (sodium nitrate?) increased both grain and straw, whilst the best result was obtained from a mixture of phosphate and nitrogen. E. W. P.

Absorption of Nitrogen by Soils. By BERTHELOT (*Compt. rend.*, **108**, 700—708).—The author's previous researches have shown that the absorption of nitrogen takes place chiefly in vegetable soils, and results in the formation of compounds of an albuminoïd character. This absorption does not take place in sterilised soils, and hence seems to be intimately connected with the life processes of microbes. It has also been shown that the total quantity of nitrogen absorbed is greatly increased when various species of leguminosæ are grown on the soil, and this conclusion is confirmed by the experiments of Franck and of Hellriegel and Wilfarth, and also by a long series of experiments, the results of which have recently been published by the author (*Ann. Chim. Phys.* [6], **16**, 433, 435, 453, 491). Three different soils were used, varying considerably in the proportion of nitrogen which they contained, and these were examined when growing no crop and also when growing each of six species of leguminosæ. They were exposed under three sets of conditions, namely, (1) with free exposure to air, (2) under a transparent cover which allowed of free circulation of air; and (3) in a closed vessel into which carbonic anhydride and purified air could be introduced at will.

In all cases there was absorption of considerable quantities of nitrogen, which in the closed vessels amounted in some cases to 11 per cent. of the original nitrogen in two months, with free exposure to 41·3 per cent. of the original nitrogen in 19 weeks, and under cover with free circulation of air to 35·8 per cent. of the original nitrogen in 21 weeks. These numbers would be larger if the nitrogen were estimated to a depth of 50 cm., since previous experiments showed that there is usually a recognisable absorption down to this depth.

Tables showing the details of the experiments are given in the complete memoir (*loc. cit.*). With the three soils growing no crop, exposed in layers 18 cm. deep in closed vessels, the quantity of nitrogen absorbed varied from 38 kilos. per hectare in 7 weeks to 87 kilos. in 8 weeks; under cover, with free circulation, from 74 kilos. per hectare in 12 weeks to 110 kilos. in 11 weeks; with free exposure, from 30 kilos. per hectare in 11 weeks to 150 kilos. in the same time. The increase was most noticeable in the case of the soil which originally contained the lowest proportion of nitrogen, and the results were affected to the greatest extent by atmospheric conditions in the soil which originally contained the highest proportion of nitrogen. The results did not vary in the same order, in the three cases, with variations in the conditions of exposure.

Leguminosæ growing in closed vessels usually gave an increase of nitrogen at least equal to that observed with the soil alone under the same conditions, but in some cases there was an actual reduction in the total nitrogen, because part of the nitrogen existing in the seeds was lost in the form of some volatile compound. With free exposure to air, or under cover with free circulation, the quantity of nitrogen absorbed with leguminosæ growing on the soils was from two to three times as great as that absorbed by the same soils under the same conditions without plants, and from two to three times as great as the absorption with the same plants in closed vessels. The relative increase was greatest with the soil originally containing the least nitrogen, but the magnitude of the absolute increase was of the same order in all three cases. A considerable proportion of the nitrogen is absorbed by the plant, the quantity in the latter becoming two or three times as great as the quantity present in the seed. The quantities absorbed by the sub-aerial and subterranean parts of the plant respectively are approximately equal. It would seem that the nitrogen is actually absorbed from the soil by the roots of the plants under the influence of microbes. A simultaneous enrichment of both the plant and the soil does not always take place; in some cases the quantity of nitrogen in the plant increases, whilst that in the soil diminishes. There is at present no evidence that the tubercles on the roots, which undoubtedly contain microbes, play any special part in bringing about this result. At the same time, the absorption of nitrogen does not take place solely, nor even in a preponderating degree, with the lower orders of vegetation. The assumption that the absorption takes place through the agency of microbes is based mainly upon the facts that it is not observed with sterilised soils, that the nitrogen is converted into substances of an albuminoid character, and that, as Hellriegel and Wilfarth observed, an infusion of a vegetable soil will restore to a sterilised soil the property of fixing nitrogen.

The question of the absorption of nitrogen by the sub-aerial portions of plants requires further investigation. The author has proved by direct experiments that carbohydrates, which make up the greater part of vegetable structures, combine directly with nitrogen under the influence of low tension electricity such as is found in the atmosphere in contact with and immediately above the soil.

The quantities of nitrogen which are absorbed by soils growing leguminosæ are very considerable, and would have been still greater if the experiments had been continued for a longer time, but probably tend to a maximum limit.

The soils growing lucerne showed the greatest increase of nitrogen, which amounted to as much as 700 kilos. per hectare in five months. The soil in this case contains only one-third to one-quarter of the total nitrogen in the system, whilst the nitrogen in the lucerne is 16 times as great as that originally present in the seeds. The greater part of the absorption is done by the roots of the lucerne, which also absorb a very large quantity of mineral matter from the soil.

C. H. B.

Loss and Gain of Nitrogen in Soils. By P. P. DEHÉRAIN (*Compt. rend.*, **108**, 873—878).—Experiments which have been conducted with a somewhat loose sandy soil at Grignon since 1878, have shown that when the soil is cultivated for several years without any application of manure, there is a considerable loss of nitrogen, the loss being much greater than the quantities of nitrogen removed in the crops. The magnitude of the loss varies with the nature of the crop, and is most rapid with beet, slower with maize for forage, and still slower with potatoes and wheat. After several years under these conditions, the nitrogen was reduced to 1·45—1·5 grams per kilo. It was then found that the loss of nitrogen ceased and a gain of nitrogen set in. This gain was only moderate with many crops, but was very considerable with crops of sainfoin and grasses. C. H. B.

Comparison of Basic Slag with Superphosphate. By E. MEISSL (*Bied. Centr.*, 1889, 228—229).—The experiments were conducted in 30 different districts, the ground receiving, in addition to the phosphates, a dressing of ammonium sulphate. The yield produced by the basic slag was higher than that by superphosphate, the crops being wheat (winter and spring) and rye, hay and oats, and the phosphoric acid of the slag being added to the amount of 2½ times that of the "super." E. W. P.

Analytical Chemistry.

Behaviour of Phenolphthaleïn with Ammonia. By J. H. LONG (*Amer. Chem. J.*, **11**, 84—89).—When phenolphthaleïn is added to weak sodium hydroxide solution, the red colour seems to be indefinitely permanent; but with weak ammonia it disappears more or less quickly, the chief determining factors being dilution, temperature, and strength of the indicator.

A similar result is observed when sodium hydroxide is added to a solution of free acid containing some ammonium salt and the indicator; in this case, if the temperature is sufficiently low, very little error will be caused by small quantities of ammonium salts, but with larger quantities the error is too great, unless a large quantity of the indicator be used.

The author's experiments lead him to conclude that the fading of the colour is due to the formation of the colourless phenoldiimidophthaleïn described by Baeyer. A. G. B.

Estimation of Organic Nitrogen. By L. L'HOTE (*Compt. rend.*, **108**, 817—820).—The nitrogen in brucine, cinchonine, asparagine, caffeïne, oxamide, uric acid, and urea was determined by means of soda-lime, and also by Kjeldahl's process as described in the *Encyclopédie chimique*, **4**, 48. In those cases where the sulphuric acid became colourless, the results were exact, and agreed with those obtained with soda-lime, but when, as in the case of brucine and cinchonine. the acid remained brown, the results were considerably too low. Blood, caseïn, and wheat when boiled rapidly with sulphuric acid for about an hour and a half give an almost colourless solution, but a considerable quantity of the ammonium salt is volatilised, and the results are too low. The author concludes that Kjeldahl's process has no advantage over the soda-lime method in simplicity, rapidity, or accuracy.

The author finds that, contrary to a recent statement by Cazeneuve and Hugounenq, albumin and the residue from urine give with soda-lime results identical with those obtained by Dumas' method with cupric oxide. C. H. B.

Estimation of Nitrogen in Nitrates by Kjeldahl's Method. By O. FOERSTER (*Chem. Zeit.*, **13**, 229—230).—In using the method previously suggested (this vol., p. 547) the thiosulphate must not be added before the phenolsulphonic acid, nor should the latter contain more than 7 or less than 4 per cent. of phenol. The object of the thiosulphate is to convert the nitrogen into a non-volatile form according to the equation:—$4H_2SO_4 + 4HNO_3 + Na_2S_2O_3 = 4SO_4(NO_2)HO + 2NaHSO_4 + 3H_2O$, therefore cooling is now stated to be unnecessary. After treating with the thiosulphate, 10 c.c. of pure sulphuric acid and sufficient mercury are added and the mixture heated before adding soda, &c.

By using a bulb apparatus for absorbing the ammonia, loss by non-absorption is avoided. D. A. L.

Estimation of Insoluble Phosphates. By V. EDWARDS (*Chem. News*, **59**, 159).—5 grams of superphosphate is extracted with water, and the residue treated for half an hour on a water-bath with dilute nitrohydrochloric acid; the solution is filtered, mixed with 20 c.c. of a solution of calcium phosphate in dilute nitric acid (containing 5 grams $Ca_3P_2O_8$ per litre), and made up to 250 c.c. 50 c.c. of this solution is made alkaline with ammonia, acidified with acetic acid, and titrated with uranium solution, being heated to boiling at the start of the titration. Allowance must be made for added phosphate and for iron and alumina. D. A. L.

Reaction for Copper. By DENIGÈS (*Compt. rend.*, **108**, 568).—The copper salt is converted into the bromide by the action of potassium bromide, and when the product is dehydrated by sulphuric acid, the solution of the copper salt in excess of potassium bromide acquires a red-violet coloration. C. H. B.

Volumetric Estimation of Nickel. By T. MOORE (*Chem. News*, **59**, 160).—The following method for estimating nickel, in which cupric ferrocyanide is used as an indicator, is recommended as trustworthy and quite accurate enough for ordinary purposes. The cupric ferrocyanide is prepared by dissolving 2·25 grams of copper sulphate in a litre of water, and adding a solution of potassium ferrocyanide until a precipitate ceases to form; it is agitated before use.

The solution containing nickel, if acid, is made strongly alkaline with ammonia, but if it already contains much free ammonia, part of this is neutralised with hydrochloric acid, a solution containing 22·5 grams of pure potassium cyanide per litre is run in until the blue colour completely disappears and the solution becomes yellow, a measured quantity of the cupric ferrocyanide, sufficient to give a distinct colour, is then added, and more potassium cyanide is run in cautiously until finally one drop causes a distinct change of colour in the solution. The potassium cyanide is standardised with a nickel solution of known strength; generally 20 c.c. = about 0·1 gram of nickel; the quantity of potassium cyanide required to decolorise, the cupric ferrocyanide may as a rule be neglected, but, if desired, can be readily ascertained by direct titration. The process works equally well in the presence of sulphates, nitrates, chlorides, acetates, and ammonium salts. D. A. L.

Estimation of Nickel and Cobalt. By A. CARNOT (*Compt. rend.*, **108**, 610—612). See p. 678.

Separation of Nickel and Cobalt. By A. CARNOT (*Compt. rend.*, **108**, 741—744).—If bromine is added to a cold solution of a nickel or cobalt salt containing free acid or ammonium chloride, and the liquid is afterwards saturated with ammonia, gas is evolved, and the solution acquires a pale-rose colour if cobalt alone is present, or a violet colour if the liquid also contains nickel.

If hydrogen peroxide is added to the cold liquid either before or after saturation with ammonia, a brown coloration is produced, which soon changes to purple and then to rose, the changes taking place more rapidly in hot solutions. The pink colour of the cobalt is much less intense when the liquid is hot, whilst the blue colour due to nickel is not affected, and this difference may be utilised for the detection of the two metals. By prolonged boiling, the purpureo-cobalt salt which has been formed is converted into a luteo-cobalt salt, and the liquid becomes turbid, the final product being the sesquioxide Co_2O_3, which, however, is not pure, but contains nickel.

When the cold solution which has been treated with hydrogen peroxide is mixed with a sufficient excess of potassium hydroxide, depending on the quantity of ammonia and ammonium salts present, the whole of the nickel is precipitated. The precipitate, however, is never pure, even with considerable variations in the conditions, and in order to obtain accurate results it must be redissolved and the treatment repeated once or twice. The cobalt in the filtrate is precipitated by prolonged treatment with hydrogen sulphide, or by addition of ammonium sulphide. C. H. B.

Estimation of Glycerol in the Residues of Brandy Distillation. By H. v. TÖRRING (*Landw. Versuchs-Stat.*, **36**, 29—60).—See p. 735.

Estimation of Glycerol in Crude Glycerol. By J. LEWKOWITSCH (*Chem. Zeit.*, **13**, 93 and 191—192; also F. FILSINGER (*ibid.*, 127).—Lewkowitsch advocates Benedict and Cantor's acetin method, and finds it gives good results even with moderately impure glycerol. He criticises various other methods, regards purification with lead acetate as untrustworthy, and disapproves of Morawski's method. Filsinger, on the other hand, has not found the acetin method so good; criticises Lewkowitsch, and commends the permanganate method for all but very bad glycerols containing much acroleïn and little glycerol. D. A. L.

Separation of Strychnine from Brucine. By J. E. GEROCK (*Arch. Pharm.* [3], **27**, 158—162).—The alkaloïds are gently warmed, and precipitated from a solution as nearly neutral as possible by means of picric acid. After remaining for some time, the precipitate is collected on a tared filter, washed with cold water, dried at 105°, and weighed. The filtrate is warmed for some time with nitric acid of sp. gr. 1·056, the solution is exactly neutralised, and a trace of acetic acid added; after cooling completely, the insoluble strychnine picrate is brought on to the same filter as before, washed, dried, and weighed. From the difference in weight, the brucine is calculated. The numerical results given are satisfactory. J. T.

General and Physical Chemistry.

Variation with Temperature of the Velocity of Light in Metals. By A. KUNDT (*Ann. Phys. Chem.*, [2], **36**, 824—833).—In a former communication on the indices of refraction of metals (Abstr., 1888, 997), the author showed reasons for believing in the existence of a relation between the velocity of light in metals and their conducting powers for electricity and heat. At the end of this paper it was pointed out that if a simple relation really existed between the velocity of light in a metal and its conductivity for electricity and heat, then the former quantity would necessarily vary with the temperature. The variation with the temperature in the conductivity for heat of different metals appears to be somewhat variable. According to Arndtsen, the electrical conductivity in pure solid metals decreases by about 0·003678 for an increase of 1° C. in the temperature. Clausius has pointed out that this is very nearly the same as the coefficient of expansion of a perfect gas; from which it would follow that the conductivity for heat is in all solid metals inversely proportional to the absolute temperature.

Siemens (*Gesammelte Abhandl.*, 259) suggests that the slight deviations from this law are probably due to a want of absolute chemical purity in the metals, and to the fact that some of the specimens experimented with were not completely annealed. With the exception of some minor modifications, the measurements were made in the same manner as those described in the paper previously referred to. Prisms of gold, platinum, nickel, iron, and silver were experimented with. Let μ_1 and μ_2 be the indices of refraction at the temperatures t_1 and t_2 respectively; then the author expresses the relation between the index of refraction and the temperature in the form

$$\mu_2 = \mu_1\{1 + \beta(t_2 - t_1)\}.$$

The values obtained for β are as follows:—

For gold with red light	0·0035
„ gold with blue light	0·0051
„ platinum with white light	0·0027
„ nickel with red light	0·0026
„ iron with red light	0·0040
„ silver with white light	0·0064

The author states that the value of β obtained in the case of silver cannot be depended on, because, owing to its very small index of refraction, the change in the deviation with the temperature is so small as hardly to exceed the limits of errors of observation. Except in the case of silver, the author considers that the values obtained for β agree very well with the temperature coefficient for electrical resistance, although of course it is a matter of chance that the mean of the former values, viz., 0·0036, is almost identical with the mean of the latter. The deviations of the different values of β from this mean are, however, quite within the limits of errors of observation, and therefore, as far as the observations go they indicate that the indices of refraction of metals have a constant temperature coefficient, 0·0036; or in other words, that the velocity of light in any given metal is inversely proportional to the absolute temperature; which is exactly the same relation as that which Lorenz, Arndtsen, and Benoit have found to exist between the absolute temperature and the electrical conductivity. Matthiessen, also, who expressed the variation of electrical conductivity with temperature by means of two terms, one proportional to the temperature, and the other proportional to its square, gives 0·003764 as the mean coefficient of the first member, obtained from experiments on 10 different metals.

The author's experiments therefore appear to show that the velocity of light at different temperatures in a given metal is directly proportional to the electrical conductivity. He expresses his intention of continuing his investigations with more perfect prisms, and in measuring the index of refraction and the electrical conductivity for the same specimens of metal. The author does not consider that the experiments afford any trustworthy proof of an alteration with temperature in the dispersion of light by metals, for although the values obtained for β in the case of gold were 0·0035 with red light and 0·0051 with white light, the difference may quite possibly be due merely to errors of observation. G. W. T.

Variation in the Specific Heat of Mercury with Temperature. By J. Milthaler (*Ann. Phys. Chem.* [2], **36**, 897—911).—The author finds that, as has been previously shown by Naccari (*Mem. R. Acad. Torino*, 1888), the specific heat of mercury decreases with increasing temperature. If C_0 is the specific heat of mercury at 0° and C_t is the specific heat at the temperature t, he obtains the following formula, expressing the relation between the specific heat and the temperature: $C_t = C_0(1-0\cdot000138t)$.

G. W. T.

Isotherms of a Mixture of Sulphurous and Carbonic Anhydrides. By A. Blümcke (*Ann. Phys. Chem.* [2], **36**, 911—923).—In a former paper (Abstr., 1888, 775), the author described a series of experiments tending to show that a mixture of sulphurous and carbonic anhydrides does not behave like the saturated vapour of a single liquid.

He points out that this is a matter of considerable importance, as in calculating the efficiency of freezing machines the pressure of the vapour is employed for determining the temperature. It is also of importance on account of theoretical applications, as for example to the proof of the second law of thermodynamics.

To decide definitely whether the vapour-pressure depends only on the temperature, or whether it also depends on the relative volumes, the author has obtained a series of curves representing the relation between pressure and volume at different temperatures, and a noteworthy feature of these is that they undergo no sudden variation corresponding with the commencement of condensation, but throughout closely resemble the isotherms for permanent gases. The isotherms are in no part parallel to the axis of volumes, and therefore it is not permissible to employ the vapour-pressure for the determination of the temperature unless the volume is known with exactness.

At the conclusion of his paper, the author traverses in detail the objections advanced by Pictet against the method of observation employed in the experiments described in the paper previously referred to. G. W. T.

Gas Heating. By L. Meyer (*Ber.*, **22**, 883—885).—It was found by the analysis of a sample of coal-gas by Bunsen's method that 1 litre of the gas gives approximately three-fourths of the heat evolved by the combustion of 1 gram of coal.

The results of analyses of coal-gas or any gaseous mixture are always given in volumes, whilst the heat of combustion is given either for one part by weight or for the molecular weight of each constituent, and the calculation of one from the other is a very tedious process.

Since the molecular weight, in grams, of any gas occupies 22·312 litres at 0° and 760 mm., if a gaseous mixture contains in one volume a fraction x of any one constituent, this fraction of the molecular weight is present in 22·312 litres. It is, therefore, only necessary to multiply the molecular heat of combustion of each constituent by the quantity of this constituent in one volume to find what portion of the heat evolved by 22·312 litres of the gaseous mixture is due to the constituent in question. For example, if a mixture contains 34·02 per cent. by volume of methane, one volume contains 0·3402 volume and, therefore, 22·312 litres contain $0·3402 \times 16$ grams; as the heat of combustion of 16 grams of methane is 211,930 cal., the above quantity of marsh-gas would give $211930 \times 0·3402 = 72099$ cal. In this way the heat evolved by each constituent is readily calculated, and if the sum is divided by 22·312 the quotient gives the heat of combustion of 1 litre of the gaseous mixture at 0° and 760 mm. F. S. K.

The Absorption and Condensation of Carbonic Anhydride on Clean Glass Surfaces. By H. Krause (*Ann. Phys. Chem.* [2], **36**, 923—936).—The author states that the investigation described in this paper was suggested by a remark made by Warburg and Ihmori in a paper (*ibid.* [2], **27**, 481) on the "Weight of the Layer of Water formed on Glass and other Bodies, and the Circumstances under which it is formed." The remark was to the effect that it would be interesting to ascertain whether glass free from alkali absorbs a sensible quantity of carbonic anhydride. In the present paper, the author shows that by treating glass with boiling water the greater part of the alkali can be removed from its surface, and he finds that glass fibres in their natural condition are able to condense a much larger amount of water, and to retain it much more firmly, than those which have been treated in this manner. The principal results attained in the course of the investigation are as follows:—

(1.) When the surface of the glass is perfectly dry, scarcely any condensation or absorption of carbonic anhydride takes place, even when the glass is exposed to the gas for a considerable time. This holds good both when alkali is present on the surface and when it has been removed as far as possible by treatment with boiling water.

(2.) When the dry surface of the glass is moistened, a condensation of gas upon the surface immediately begins, and this condensation is greater when the alkali is present than when it has been as far as possible removed. In either case the condensation takes place very rapidly at first. Since the condensation and absorption take place in both cases, the question propounded by Warburg and Ihmori is answered.

(3.) When the temperature is gradually raised, the amount of water retained on the surface is greater when alkali is present than when the fibres have been previously boiled. In the case of the boiled fibres, moreover, the moisture can be removed more rapidly or at a lower temperature by means of a dry current of air than when alkali is present in the normal quantity. G. W. T.

Conditions of Equilibrium between Solid and Liquid Compounds of Water with Salts, particularly with Calcium Chloride. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **8**, 1—146).—The object in view was to make a complete investigation of the conditions of equilibrium between a single salt, calcium chloride, and water, and also to test the deductions of Van der Waals with reference to the conditions of equilibrium of two substances (Abstr., 1887, 629).

The compounds of calcium chloride with water which are capable of existing in the solid state are found to be: $CaCl_2 + 6H_2O$, $CaCl_2 + 4H_2O(\alpha)$, $CaCl_2 + 4H_2O(\beta)$, $CaCl_2 + 2H_2O$, and $CaCl_2 + H_2O$. Each of these hydrates can only exist between certain limits of temperature which lie between −55° and +260°, the lower temperature being that at which the cryohydrate is formed, the higher temperature the melting point of anhydrous calcium chloride. Each hydrate has a curve of solubility of its own, the upper limit being for each, except the first, the temperature at which the hydrate fuses. In the case of $CaCl_2 + 6H_2O$, the hydrate can also exist in a solution containing less water than the solid salt. These solubility curves therefore cut one another in the points of fusion of the hydrates, at which points two hydrates are capable of existing in the same solution and in equilibrium. As these points of intersection are definitely and clearly marked, the transition from one hydrate to another in solution by increasing or decreasing the degree of hydration is a sudden and not a gradual operation.

The curves for the vapour-pressures of various solutions of calcium chloride in water are also given. These intersect in quadruple points, each of which corresponds with equilibrium between four phases (Abstr., 1888, 1151), the two hydrates, the solution, and aqueous vapour. The positions of these points together with the phases present for each are as under :—

t.	*p.*	Phases present.			
	mm.				
−55·0°	±0	Ice	$CaCl_2 + 6H_2O$	$CaCl_2 \approx 14·5H_2O$	Aq. vapour.
+29·2	5·67	$CaCl_2 + 6H_2O$	$CaCl_2 + 4H_2O (\beta)$	$CaCl_2 \approx 5·41H_2O$	,,
29·8	6·80	$CaCl_2 + 6H_2O$	$CaCl_2 + 4H_2O (\alpha)$	$CaCl_2 \approx 6·10HO_2$	,,
38·4	7·88	$CaCl_2 + 4H_2O (\beta)$	$CaCl_2 + 2H_2O$	$CaCl_2 \approx 4·83H_2O$	,,
45·3	11·77	$CaCl_2 + 4H_2O (\alpha)$	$CaCl_2 + 2H_2O$	$CaCl_2 \approx 4·73H_2O$	,,
175·5	842·0	$CaCl_2 + 2H_2O$	$CaCl_2 + H_2O$	$CaCl_2 \approx 2·07H_2O$	,,
±260·0	several atmos.	$CaCl_2 + H_2O$	$CaCl_2$	$CaCl_2 \approx \pm 1·8H_2O$	,,

The curves are compared with the ideal curve deduced from the formula of Van der Waals for the equilibrium of two substances in three phases mentioned above. The results are found to be in agreement with those required by the theory.

The numbers obtained for the vapour-pressures are also used for confirming the relation given by Kirchhoff and modified by Van der Waals, as existing between vapour-pressure and heat of dissolution. This relation has the form—

$$\frac{d \log p}{dt} = \frac{(x - c)q + Q_c^x}{2T^2(x - c)},$$

where Q_c^x is the heat evolved by the dissolution of $CaCl_2 \approx xH_2O$ to $CaCl_2 \approx cH_2O$, and q is the heat of condensation of 1 mol. of water. Using Thomsen's thermochemical data it is found to hold good for saturated solutions of $CaCl_2 + 6H_2O$, and an agreement is also apparent for the lower hydrates. H. C.

Unit of Atomic Weights. By L. MEYER and K. SEUBERT (*Ber.*, **22**, 872—879). The authors are of opinion that all determinations of the ratio of the atomic weights of oxygen and hydrogen, depending on the weighing and measuring of the gaseous elements, are attended with considerable errors, as is shown by the discordant results of numerous experimenters. The average of the results obtained by Brauner (this vol., p. 335), namely O = 15·94, although approximately correct, is still a little too low, as 15·96 is the most trustworthy value for the atomic weight of oxygen.

Marignac and Brauner, although apparently admitting the ratio O : H = 15·96 : 1, are in favour of making the atomic weight of O = 16 and that of H = 1·0025. Although the proportionate values of those atomic weights, calculated directly from that of oxygen, remain the same whatever the ratio of O : H, it is stated that if oxygen were taken as 16, the atomic weights of many elements could, without appreciable error, be regarded as whole numbers and thus facilitate the calculation of analyses. The authors show by a table that such is not the case, and state that in their opinion the proposal to take the atomic weight of O = 16 as the standard is not based on sufficiently good grounds to necessitate a departure from the most natural unit H = 1. F. S. K.

Raoult's Method for Determining Molecular Weights as used to distinguish between Isomerism and Polymerism. By R. ANSCHÜTZ (*Ber.*, **22**, 980—983).—A reply to Auwers and Meyer (*Ber.*, **21**, 3510).

Air-baths. By L. MEYER (*Ber.*, **22**, 879—883).—The author describes, with the aid of diagrams, several improvements in the construction of various forms of hot-air baths (compare *Ber.*, **16**, 1807) suitable for heating flasks, retorts, &c., and for evaporating aqueous solutions. F. S. K.

Lecture Experiments. By P. T. AUSTEN (*Amer. Chem. J.*, **11**, 270—273).—The author describes an apparatus for showing the combination of nitric oxide and oxygen, and the solubility of nitric peroxide in water. He also describes some experiments with hydrogen iodide; heated potassium chlorate, nitric acid gas, and chlorine, all burn in this gas; nitrous oxide is converted by it into ammonium iodide; sulphurous anhydride decomposes it. A. G. B.

Inorganic Chemistry.

Formation of Hydrogen Bromide and Hydrogen Iodide. By V. MERZ and E. HOLZMANN (*Ber.*, **22**, 867—872).—The synthesis of hydrogen bromide from its elements (compare Merz and Weith, this Journal, 1874, 334) can be demonstrated by passing dry hydrogen through a fractionating flask containing boiling bromine, and conducting the gaseous mixture through a tube provided with one or two bulbs and heated at the commencement of the operation for a short portion of its length. Combination takes place and tongues of flame two or more inches long are visible in the tube; in presence of excess of hydrogen the flame is distinctly yellow. Another method is to place a hydrogen flame near the mouth or into the neck of a flask of about 1 litre capacity, containing boiling bromine; the size of the flame is thereby considerably increased. The best method, however, is to introduce a hydrogen flame into a flask containing bromine and filled with oxygen and then heat immediately; hydrogen bromide is formed, and as long as the supply of bromine is kept up the size of the flame is greatly increased.

Colourless fuming hydrobromic acid can be prepared by the above reaction (compare Harding, Abstr., 1882, 138). A rapid stream of hydrogen is passed into a flask containing boiling bromine, the mixed vapours, conducted first through a short combustion-tube containing broken glass covered with charcoal, and heated to dull redness, then into a Woulf's bottle, into which a second stream of hydrogen is passed, and finally through a heated glass tube into cold water.

When hydrogen and iodine vapour are passed through a red-hot tube containing pumice, a considerable quantity of the iodine is converted into hydrogen iodide, and if the escaping gas is filtered through cotton-wool and passed into cold water, colourless hydriodic acid is obtained. Experiments were made to determine the quantity of hydrogen iodide formed in a given time from a given quantity of iodine at various temperatures. The results showed that the higher the temperature the larger the quantity of hydrogen iodide produced.

Sodium is not acted on when heated at 200°, 250°, or 300° with pure bromine or with bromine containing considerable quantities of iodine; iodine alone has also no action on sodium at 350—360°.

Some sodium which has been kept in bromine since 1873 still retains its metallic lustre. F. S. K.

Solubility of White Precipitate in Solution of Ammonia containing Ammonium Carbonate. By G. S. JOHNSON (*Chem. News*, **59**, 234).—The author finds that ammonium carbonate is far more potent than ammonium chloride in preventing the precipitation of mercuric chloride by ammonia; in fact, even after complete precipitation of a solution of mercuric chloride by ammonia, the addition of ammonium carbonate causes the precipitate to redissolve.

Ammonia solution kept in loosely stoppered bottles is liable to absorb carbonic anhydride from the air, and hence become unfit for the above precipitation. D. A. L.

Crystalline Form of Metallic Zinc. By G. H. WILLIAMS and W. M. BURTON (*Amer. Chem. J.*, **11**, 219—227).—By unequally heating a tube containing the metal, three types of zinc crystals were obtained, namely, (1) spheroidal polyhedral aggregates, (2) barrel-shaped crystals, and (3) tabular hexagonal plates. These three types are described and figured in the paper; only the third furnished crystallographic data, and the axial ratio of this type is given as $a : c = 1·356425$. Observed faces 0P, $\frac{4}{7}$P, $\frac{2}{3}$P, P, $\frac{3}{2}$P, 6P, ∞P, $\frac{5}{2}$P, $\frac{8}{3}$P, 4P, $\frac{13}{3}$P. Very perfect cleavage takes place parallel to the basal pinacoïd. No rhombohedral cleavage can be traced; striations similar to those observed by Rose, and intersecting at 60°, were obtained, but these were found to be pressure-lines produced by cleavage.

The analogy of the axial ratio of zinc to that of arsenic, antimony, bismuth, and tellurium supports the accepted view that the metal is rhombohedral, although the crystals measured by the authors do not definitely prove the assumption. A. G. B.

Dissociation of the Oxides of Zinc and Cadmium in the Vapours of their Respective Metals. By H. N. MORSE and J. WHITE (*Amer. Chem. J.*, **11**, 258—263).—When heating zinc oxide in a current of hydrogen, Deville observed a deposition of some of the oxide further on in the tube, and concluded that the oxide was first reduced by the hydrogen with the formation of water, and that the metal afterwards reduced the water, with reformation of zinc oxide, at a point of the tube where the temperature happened to be higher. Subsequent experiments by Deville and Troost showed a similar transference of zinc sulphide in a current of hydrogen. Neither of these cases can be a simple sublimation, for zinc oxide and sulphide do not sublime in a current of inert gas.

The authors show that Deville's explanation is untenable, and propose, as an alternative, that the oxide and sulphide are dissociated under the influence of the excess of hydrogen, and are re-formed at other points of the tube where the hydrogen, owing to its smaller quantity or lower temperature, is unable to overcome the attraction of the metal for sulphur or oxygen. The intermediate formation of water or hydrogen sulphide need not be supposed.

In support of this view, the authors have succeeded in effecting the dissociation of zinc oxide by zinc, and cadmium oxide by cadmium. Having first proved that these oxides do not dissociate or volatilise in a vacuum at the softening point of glass, a mixture of the oxide and metal was placed in the end of a sealed hard glass tube provided with an indentation at one-third from the closed end to form a dam to prevent the metal from flowing. The open end having been connected with a Sprengel pump, the tube was exhausted and heated for two-thirds of its length in a combustion-furnace. Soon after the metal had fused, some oxygen was collected from the pump, and a deposit of oxide had formed before the dam. This deposit gradually disappeared, being driven before the distilling metal until it reached the cool part of the tube, where it continued to deposit as long as any metal was left behind the dam. To cause the deposition of oxide to begin again, the back part of the tube was cooled, thus causing the metal to distil back to the oxide still left behind the dam, where it was again heated. Figures are quoted showing that when zinc oxide was used 3, 8, and 10 grams respectively were transported in three experiments.

It would appear that the atoms of the free metal attract the combined oxygen sufficiently to cause the dissociation of the oxide and the existence of nothing but free oxygen and zinc in the tube; but where the temperature is lower or the oxygen in excess (due to more rapid diffusion) the reformation of oxide occurs. A. G. B.

Some Phosphates of Polyvalent Metals. By K. R. JOHNSON (*Ber.*, 22, 976—980).—Madrell first observed that insoluble metaphosphates are formed when anhydrous sulphates or nitrates are dissolved in metaphosphoric acid at 316° (*Annalen*, 61, 53). The salts described in the present paper were prepared by Madrell's method; the phosphoric acid was heated in a platinum dish until the latter began to acquire a red heat; the dry sulphate was added until it no longer dissolved readily, and the mixture was then heated until the whole of the sulphuric acid was driven off, when it was allowed to cool slowly. The phosphoric acid was extracted with water.

Lanthanum metaphosphate, $La_2O_3,5P_2O_5$, forms clear, monoclinic plates; $a : b : c = 1·44604 : 1 : 0·95897$; $\beta = 89° 28' 20''$. Sp. gr. = 3·241. Molecular volume = 322.

Cerium metaphosphate, $Ce_2O_3,5P_2O_5$, forms microscopic crystals. Sp. gr. = 3·272; molecular volume = 317. Both salts are insoluble in acids.

Uranium phosphate, $UO_3,2P_2O_5$, crystallises in green, microscopic, rectangular plates. Sp. gr. = 3·818; molecular volume = 149.

Ferric metaphosphate, $Fe_2O_3,3P_2O_5$. Sp. gr. = 3·020; molecular volume = 194. Somewhat soluble in strong sulphuric acid.

Chromium metaphosphate, $Cr_2O_3,3P_2O_5$. Sp. gr. = 2·974; molecular volume = 195.

Aluminium metaphosphate, $Al_2O_3,3P_2O_5$. Sp. gr. = 2·779; molecular volume = 190.

Yttrium pyrophosphate, $2Y_2O_3,3P_2O_5$, forms white, microscopic, hexagonal plates, insoluble in acids. Sp. gr. = 3·059; molecular volume = 288.

Thorium metaphosphate, $ThO_2,2P_2O_5$. Microscopic rectangular plates. Sp. gr. = 3·922; molecular volume = 140. (Compare Hautefeuille and Margottet, Abstr., 1886, 670.) N. H. M.

Molecular Weight of Aluminium Compounds. By ROUX and E. LOUISE (*Bull. Soc. Chem.*, **50**, 497—516).—After referring to the contradictory results obtained in previous investigations on this subject (Deville and Troost, *Ann. Chim. Phys.* [3], 58, 276 and 279; Buckton and Odling, *Proc. Roy. Soc.*, **14**, 19; Nilson and Pettersson, Abstr., 1888, 788; Friedel and Crafts, *ibid.*, 1040), the authors observe that in all these cases the more complex molecules exist at low temperatures, and these dissociate more and more as the temperature rises, causing a gradual decrease in the density. The decomposition even goes further, as in the authors' experiments to be later described. V. Meyer also (Abstr., 1888, 422), in determining the density of ferric chloride, found considerable quantities of ferrous chloride and free chlorine in his apparatus, even after it had cooled down.

The authors have examined the vapour-densities of aluminium-methyl and aluminium-ethyl by V. Meyer's method in an atmosphere of nitrogen; they prepared these substances by heating mercury methyl (or ethyl) with aluminium in a sealed tube and distilling in an atmosphere of nitrogen, and obtained the following results:—

Aluminium - methyl (b. p. 140°) ……	182°	216°	310°	350°	440°
Vapour-density …..	74	68	66	35	24

Theory for Al_2Me_6 = 72·4; for $AlMe_3$ = 36·2.

Aluminium - ethyl (b.p. 195—200°)..	235°	258°	310°	350°	440°
Vapour-density …..	116	92	37	36	18

Theory for Al_2Et_6 = 114; for $AlEt_3$ = 57.

The authors draw the conclusion that at temperatures little removed from the boiling point these substances possess the more complex molecular formulæ Al_2Me_6, &c.; and that as the temperature rises, dissociation takes place; it goes, however, far beyond the formation of molecules of $AlMe_3$, &c.; at 440° the densities correspond approximately with $\frac{2}{3}AlMe_3$ and $\frac{1}{3}AlEt_3$.

[The reason why Nilson and Pettersson never obtained a density corresponding with Al_2Cl_6 for aluminium chloride is that they started with a temperature of 440° = 250° above its boiling point.]

The authors have also determined by Raoult's method the molecular weights of aluminium ethyl, propyl, and isoamyl in solution in ethylene bromide, by observing the lowering of the freezing point (which was read to $\frac{1}{100}$ degrees) of these solutions; they operated in an atmosphere of nitrogen. Three experiments gave as freezing point 9·73°, 97·4°, and 9·75°. Raoult's data for this solvent being scanty, the authors determined the constant "molecular lowering" by dissolving several substances in it; they find a number closely agreeing with that of Raoult, who found 118°, using substances different from those used by the authors. They obtained a rather higher number by dissolving in ethylene bromide certain organo-compounds of mercury; but these substances were impure; hence they take 118 as the correct number.

Aluminium-ethyl, aluminium-propyl, and aluminium-isoamyl were obtained by heating the corresponding mercury compound with aluminium in a sealed tube and redistilling in an atmosphere of nitrogen (in the case of the isoamyl compound, under reduced pressure).

Aluminium-ethyl (b. p. 195—200°).

Molecular lowering found	112·7	115·2	118·9;	if formula = Al_2Et_6
	56·3	57·6	59·4;	if formula = $AlEt_3$

Aluminium-propyl (b. p. 250°).

Molecular lowering found	89·2	91·1	91·4	92·6	99·8;	if formula = $Al_2Pr_6^{\alpha}$.
	44·6	45·5	45·7	46·3	49·9;	if formula = $AlPr_3^{\alpha}$.

Aluminium-isoamyl (b. p. 250° at 100 mm.).

Molecular lowering found	83·2	84·7	85·6;	if formula = $Al_2(C_5H_{11}^{\beta})_6$.
	41·6	42·3	42·8;	if formula = $Al(C_5H_{11}^{\beta})_3$.

The normal molecular lowering is 118; hence it is evident that the formula of the above substances must be written on the type Al_2X_6, and not AlX_3, as well from determinations of the freezing point of their solutions as from their vapour-densities. (Compare also Combes, this vol., p. 571; Quincke, *ibid.*, 695.) C. F. B.

Note.—For summary of these and similar results up to the early part of 1889, see paper by Young in *Nature*, **39**, 198; also discussions of these results by Brauner, *ibid.*, 318, and Young, *ibid.*, pp. 319 and 536. C. F. B.

Green Ultramarine. By J. Szilasi (*Annalen*, **251**, 97—114).—The author finds that green ultramarine from three distinct sources has the same composition, and further that by the action of certain metallic salts the sodium in green ultramarine can be displaced by equivalent quantities of silver, lead, or zinc. W. C. W.

Atomic Weight of Nickel and Cobalt. By C. WINKLER (*Ber.*, **22**, 890—899).—Krüss and Schmidt (this vol., p. 349) have stated that it is impossible to precipitate an equivalent quantity of gold from a neutral solution by means of nickel and cobalt, and as the author had previously employed this reaction in his investigations on the atomic weights of nickel and cobalt, he has repeated some experiments in order to find the explanation of the difference between his own and Krüss and Schmidt's observations.

Gold, precipitated with sulphurous acid, washed, and dried at 180°, was treated at 140° for several hours with chlorine which had been repeatedly washed with sodium hydrogen carbonate and water, and dried with sulphuric acid. The resulting chloride was kept for several days over potash, dissolved in water, the solution heated for a long time on the water-bath and filtered; the quantity of gold present varied in the experiments from 12 to 20 grams per litre, and the solution showed an acid reaction. When diluted to 0·4 gram of gold per litre and treated gradually with dilute sulphurous acid, an intense cherry-red coloration was produced (compare Kruss and Schmidt, *loc. cit.*), and even on boiling or on exposure to the air the colour did not change, but when the solution was kept in closed vessels gold was gradually deposited. Sometimes, however, the solution was unstable, seemingly owing to the presence of too much sulphurous acid. The red coloration was not altered by the addition of acetic acid, but traces of nitric acid, hydrochloric acid, sulphuric acid, sodium chloride, or sodium cyanide changed it first to purple and then to blue, and finally metallic gold was precipitated.

Various reactions show that the coloration is most probably due to the presence of small quantities of aurous chloride which, with a little sulphurous acid, gives aurous sulphite (compare Haase, *Zeitschr. f. Chem.*, 1869, 535).

The analysis of several solutions of auric chloride prepared as described above, gave 65·47 per cent. of gold and 34·53 per cent. of chlorine, so that such solutions containing, as they do, excess of gold cannot be employed for the determination of the atomic weight of nickel and cobalt (compare Krüss and Schmidt, *loc. cit.*).

Carefully purified gold was suspended in water and treated with pure chlorine, care being taken to exclude light and also dust particles; the solution was then evaporated to dryness, the residue dissolved in water, and the solution filtered. The filtrate had a slightly acid reaction but contained no aurous chloride, and after dilution it gave only a green coloration with sulphurous acid. The solutions contained on the average 62·55 per cent. gold and 37·45 per cent. of chlorine.

Pure sodium aurochloride can be prepared by adding a concentrated solution of freshly ignited sodium chloride (0·3 gram) to a pure neutral solution of auric chloride (= 1 gram of gold) recrystalling the double salt three times, and drying in a desiccator. A solution of the pure salt is also obtained when a solution of auric chloride, prepared by the first method given above, is treated with the calculated quantity of pure sodium chloride, heated for some time and filtered from the precipitated gold. A solution of the salt prepared by either of these methods gives no red coloration with sulphurous acid, and contains 6·48 per cent. of sodium, 54·39 per cent. of gold, and 39·13 per cent. of chlorine.

The reason why Krüss and Schmidt found that an equivalent quantity of gold could not be precipitated from its neutral solutions with nickel or cobalt, is that they employed metals which contained a small quantity of alkali or alkaline earth which it is almost impossible to get rid of completely. The metals which have been prepared by reducing the oxide (obtained by precipitating with alkalis) or by the reduction of the oxalate or chloride contain alkali, and metallic cobalt, prepared from purpureocobalt chloride which has been purified several times by recrystallisation, shows an alkaline reaction. Even cobalt and nickel which have been precipitated electrolytically seem to contain traces of alkali.

When pure nickel and cobalt are employed, the precipitated gold is perfectly pure, and this reaction can be employed for determining the atomic weight of the metals in question. F. S. K.

Crystalline Metallic Molybdates. By A. Coloriano (*Bull. Soc. Chim.*, **50**, 451—455).—On mixing a solution of a metallic nitrate with a solution of ammonium molybdate, the author obtained an amorphous precipitate in the cold, sometimes at once, sometimes after a time; its formation was greatly accelerated by heating the solution. These amorphous precipitates become crystalline on digestion with water; probably they lose water and acid, and are converted into basic molybdates. In some cases this conversion is difficult, but it takes place rapidly in the case of the zinc, manganese, and cobalt salts; these are described in the present paper. The crystals were in each case separated from any remaining amorphous matter, and dried in the air; they did not contain a trace of ammonia. They are hydrated salts; but none of the water is given off below 150°, and only at the temperature of boiling sulphur is it all expelled; it is therefore probably water of constitution. The salts of zinc, manganese, and cobalt were analysed; the water and the metal being determined. The metal was generally estimated by fusing with sodium carbonate, and converting the insoluble carbonate thus obtained into the oxide. The crystals were obtained as clusters of needles; they are but slightly soluble in water, easily in dilute acids; alkalis attack them, either when boiled or when fused with them. The zinc salt, $HO{\cdot}MoO_2{\cdot}O{\cdot}Zn{\cdot}OH$, is white and transparent; the manganese salt, $HO{\cdot}MoO_2{\cdot}O{\cdot}Mn{\cdot}OH$, is sulphur-yellow, becoming orange-red when heated; the cobalt salt, $HO{\cdot}MoO_2{\cdot}O{\cdot}Co{\cdot}OH$, is violet, and on heating loses water and becomes pink.

The author has obtained by the same method other molybdates of similar appearance; for example, those of nickel, cadmium, and iron; and also by operating in sealed tubes with the aid of heat, molybdates differing from the above in composition and crystalline form. The description of these experiments is reserved for a future paper.

C. F. B.

Phosphododecamolybdic Acid. By F. Hundeshagen (*Zeit. anal. Chem.*, **28**, 141—172).—Ammonium phosphomolybdate, dried above 130°, invariably has the composition $12MoO_3,PO_4(NH_4)_3$, whatever be the conditions of its formation, provided it is not mixed with free molybdic acid. It, however, separates from solution in combination with 2 mols. of the acid present in the liquid (HNO_3 or HCl) and 1 mol. of H_2O. These are given up at a moderate heat.

On adding ammonium nitrate to an acidified mixture of sodium phosphate and sodium molybdate, the precipitate at first redissolves, not becoming permanent until a considerable amount of ammonium nitrate has been added. The solution next becomes pale-yellow and turbid, in which state it passes unchanged through filter-paper. Addition of a little more ammonium nitrate causes the precipitate to contract and subside, leaving a clear, colourless solution, from which ammonium nitrate throws down no further precipitate. This point is reached when the solution contains between 4 and 5 grams of ammonium nitrate per litre, and is independent of the amount of the other reagents present.

On adding nitric acid to a hot, neutral mixture of the other reagents (containing 24 mols. of MoO_3 for one of P_2O_5), a permanent, yellowish coloration begins to appear when 15 mols. of HNO_3 have been added. At 17 mols. HNO_3 the first permanent turbidity appears. From 17 to 23 mols. HNO_3 the amount of precipitate increases with each addition. At 23 mols. the precipitate begins to subside, and at 26 mols. precipitation is complete. The first phase corresponds with the formation of a mixture of hexammonium diphosphopentamolybdate with hexammonium pentamolybdate according to the equation—

$$14[12MoO_4(NH_4)_2 + PO_4H(NH_4)_2] + 208HNO_3 = 7[5MoO_3,P_2O_5,3(NH_4)_2O] + 19[7MoO_3,3(NH_4)_2O] + 208NH_4NO_3 + 111H_2O.$$

The second stage appears to be the formation of a soluble ammonium phosphopentamolybdate of the formula $5MoO_3,PO_4(NH_4)_3$. In the third stage this combines with 7 mols. of MoO_3, the whole reaction occurring thus:—$12MoO_4(NH_4)_2 + PO_4H(NH_4)_2 + 23HNO_3 = 12MoO_3,PO_4(NH_4)_3 + 23NH_4NO_3 + 12H_2O$.

On further addition of acid, a point is reached at which the formation of the precipitate is hindered. Up to 80 molecular proportions no dissociation takes place; at 100 molecular proportions the filtrate contain traces; at 1900 mols. the formation of the precipitate is altogether prevented. Addition of more molybdate counteracts this tendency; the amount required is proportional to the excess of acid.

Of sulphuric acid, 23 molecular proportions are also necessary for complete precipitation. Presence of ammonium sulphate makes more acid necessary; a large amount prevents precipitation altogether. Borax also prevents precipitation, but it becomes complete on adding enough nitric acid to set all the boric acid free. The already formed precipitate is not attacked by ammonium chloride or nitrate. Water, or a highly dilute solution of an ammonium salt or of an acid, on long contact in the cold, and still more on prolonged warming, dissolves a little of the yellow precipitate, which is again thrown down by strong ammonium nitrate. If the precipitate must be washed with water, the water should be ice-cold and long contact should be avoided. The best washing fluid is a feebly acidified 5 per cent. solution of ammonium nitrate. Sodium chloride or nitrate, or the chloride or nitrate of any metal which forms a soluble phosphomolybdate, dissolves the precipitate rapidly on warming. The solution gives a precipitate with an ammonium salt. Hot water rapidly dissolves considerable quantities of the precipitate with decomposition; the solution gives a precipitate with ammonium nitrate and a further precipitate on adding nitric acid. Neutral salts of polybasic mineral acids dissolve the precipitate, on heating, to strongly acid, colourless solutions in which nitric acid reproduces the yellow compound. The salts of organic acids behave as alkalis. From the solution in a salt of a monobasic acid the compound can be again completely precipitated by nitric acid and ammonium nitrate, but from those of polybasic acids it cannot be reproduced. Mineral acids attack the precipitate on heating (even in presence of ammonium salts). The compound is reprecipitated on neutralising the excess of acid. Polybasic organic acids readily dissolve the precipitate and prevent its re-formation under all circumstances.

For the titration of phosphoric acid by molybdate, the solution of the latter should be acidified with 3 to 4 molecular proportions of nitric acid for 1 of molybdic acid, whilst the phosphate solution should be only feebly acidified. With these conditions, 1 molecular proportion of P_2O_5 is exactly precipitated by 24 of MoO_3. 10 grams of molybdic acid (or 12·262 grams of crystallised hexammonum heptamolybdate) is dissolved in excess of dilute ammonia, the solution is neutralised, then further acidified with 15 grams of HNO_3 and diluted to 1 litre: 24·3—24·5 c.c. precipitate 0·01 gram of phosphoric anhydride. For the method of titrating without filtering, the original must be consulted.

For gravimetric determinations, Finkener's method is the best. The washed precipitate is dissolved in warm dilute ammonia; the solution is evaporated until most of the ammonia is expelled, then mixed with excess of nitric acid, evaporated and heated to complete decomposition of the ammonium nitrate, the final temperature being about 180°. The residue contains 3·753 per cent. of phosphoric anhydride.

If the precipitate has been washed with neutral ammonium nitrate it may be titrated. It is stirred up with cold water containing phenolphthaleïn, and mixed with standard soda until it has completely dissolved and the liquid is red. This is then rapidly titrated back with nitric acid. 1 c.c. of N/10 soda corresponds with 0·00061739 gram of phosphoric anhydride. M. J. S.

Vanadotungstic Acid. By A. Rosenheim (*Annalen*, 251, 197—234).—The author points out that the analytical methods employed by W. Gibbs in his research on the vanadotungstates (*Amer. Chem. J.*, 2 and 8) yield erroneous results.

A boiling solution of acid sodium tungstate dissolves vanadic acid, forming an orange-coloured solution, which slowly deposits orange-coloured, monoclinic plates or prisms of the composition

$$8Na_2O,16WO_3,4V_2O_5,9H_2O + 48Aq.$$

Salts of analogous composition are formed by the action of paratungstates on vanadic acid, for example:—

$8K_2O,16WO_3,4V_2O_5,9H_2O + 24Aq$, monoclinic.
$8(NH_4)_2O,16WO_3,4V_2O_5,9H_2O + 4Aq.$
$8Ag_2O,16WO_3,4V_2O_5,9H_2O.$
$8BaO,16WO_3,4V_2O_5,9H_2O + 44Aq$, rhombic.

The free acid is prepared by slowly adding the theoretical quantity of sulphuric acid to a mixture of barium tungstate and vanadate suspended in boiling water. The acid forms a deep-violet, crystalline mass, soluble in warm water. The acid has the composition $17H_2O,16WO_3,4V_2O_5 + 24Aq$; eight of the molecules of constitution water can be replaced by bases. W. C. W.

Mineralogical Chemistry.

Phosphorus in the Ludington Mine, Michigan. By D. H. Browne (*Amer. J. Sci.*, **37**, 299—310).—The author has made some 3000 analyses of iron ore from the Ludington Mine, Iron Mountain, Michigan. These analyses were necessary in order to separate the varieties of ore that occurred intermixed in the deposit. The results of the analyses have led the author to discover a method in the distribution of phosphorus through the ore deposit. The results are well exhibited in 23 sections and plans of the mine, on which either figures indicating percentages of phosphorus in the ore removed, or isochemic lines are shown. The theory of aqueous deposit explains the marked regularity of the isochemic lines and their peculiar curves, the regular decrease of phosphorus from the hanging to foot-wall of the deposit, and the hydrated, muddy deposit next the foot-wall. B. H. B.

Zinc-bearing Aragonite from Tarnowitz. By H. Traube (*Zeit. Kryst. Min.*, **15**, 410—412).—The crystals of rhombic calcium carbonate (tarnowitzite), from the Muschelkalk of Upper Silesia, containing 2·42 to 3 per cent. of lead carbonate, invariably exhibit an external appearance differing from that of aragonite and resembling that of witherite. The author has recently received from the Friedrich's mine at Tarnowitz two specimens consisting of colourless crystals of aragonite in a yellowish-brown, calamine-bearing dolomite. In a cavity on one of the specimens, some small crystals of tarnowitzite were observed unaccompanied by aragonite. Analyses were made of (I) colourless crystals and (II) imperfectly developed crystalline crusts of aragonite, as well as of (III) the tarnowitzite. The results were as follows:—

	$CaCO_3$.	$PbCO_3$.	$ZnCO_3$.	Sp. gr.
I.	97·62	0·80	1·38	3·13
II.	98·09	0·46	1·06	2·98
III.	93·02	6·64	trace	3·29

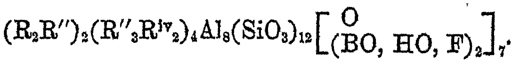
Unlike the aragonite, the tarnowitzite contains but a trace of zinc carbonate, whilst in iglesiasite there is as much as 7 per cent. of that constituent. B. H. B.

Chemical Constitution and Colour of the Tourmaline of Schüttenhöfen. By R. SCHARIZER (*Zeit. Kryst. Min.*, 15, 337—365). —In this exhaustive paper the author investigates the causes of the colour of tourmaline. He selected the tourmaline from the pegmatite granite of Schüttenhöfen for investigation, because there, in a limited area, several varieties of tourmaline occur. These present bluish-black, green, and red colours, and gave on analysis the following results:—

	SiO_2.	SnO_2.	Al_2O_3.	B_2O_3.	FeO.	MnO.	MgO.	CaO.
I.	35·10	0·07	35·10	7·09	13·36	1·48	0·98	—
II.	36·38	0·04	39·77	8·12	4·17	2·83	—	—
II.	38·49	trace	41·49	8·25	0·35	0·60	—	0·82

	K_2O.	Na_2O.	Li_2O.	H_2O.	F.	Total.
I.	0·88	1·92	—	4·01	—	99·99
II.	0·93	1·93	1·54	4·29	—	100·00
II.	2·14	1·32	1·68	4·61	0·43	100·18

I. Bluish-black tourmaline, sp. gr. 3·174; II. Green variety, sp. gr. 3·103; red variety, sp. gr. 2·913. Discussing these results and the analyses of tourmaline from other districts, the author concludes that the alkali-free and the alkali-bearing tourmalines—with the exception of the green variety—have a chemical constitution that may be expressed by the following general formula:—



$$(R_2R'')_2(R''_3R^{iv}_2)_4Al_8(SiO_3)_{12}\left[\begin{matrix}O\\(BO, HO, F)_2\end{matrix}\right]_7.$$

The reason why the green tourmaline is not in accord with this formula is probably because the degree of oxidation of the manganese is not accurately known.

On regarding the analyses of the Schüttenhöfen tourmalines, it will at once be seen that the change of colour appears to be accompanied by a change in the relative amounts of iron and manganese present, the ratios being,

In the bluish-black tourmaline,	1MnO : 8·86FeO.
,, green	1MnO : 1·45FeO.
,, red	1MnO : 0·63FeO.

It may, therefore, be concluded that with an increasing percentage of manganese the colour gradually passes from blue through green to red. Experiments made with a view to observe the behaviour of tourmaline on ignition, show that the various colours occurring in that mineral are very closely related, and that it is possible, by igniting in an oxidising flame, to convert one into another. The relative proportion of the fixed constituents, including that of manganese to iron, can thus not be the principal cause of the colour of tourmaline, for this is not altered by ignition. The degree of oxidation of the two metals is, however, changed, and this appears to be the explanation of the change of colour. B. H. B.

Formula of Tourmaline. By E. A. Wülfing (*Zeit. Kryst. Min.*, 15, 440—441, from *Tschermak's Min. Mitth.*, 10, 161).—The author calculates the chemical formula of tourmaline from the analyses published by R. B. Riggs (Abstr., 1888, 659). The formulæ of the two isomorphous molecules, to the mixture of which the varieties of tourmaline are assumed to be due, are calculated to be

I. Alkali tourmaline,

$$12SiO_2,3B_2O_3,8Al_2O_3,2Na_2O,4H_2O.$$

II. Magnesia tourmaline,

$$12SiO_2,3B_2O_3,5Al_2O_3,12MgO,3H_2O.$$

The first formula is identical with that given by Riggs.

B. H. B.

Fluocerite from Österby. By M. Weibull (*Zeit. Kryst. Min.*, 15, 431, from *Geol. Fören. Förh.*, 8, 496).—This mineral occurs at Österby, in Dalarne, Sweden, in pegmatite veins, with gadolinite and orthite. Its colour is pale orange, its sp. gr. is 5·70, and its hardness 4. Thin sections are greyish-yellow, translucent, and exhibit doubly-refracting, twinning lamellæ. The mean of four analyses gave

Ce_2O_3.	$(LaDi)_2O_3$.	Yttrium earths.	Al_2O_3.	F.	Cl.	H_2O.	$CaCO_3$.
46·03	36·00	3·96	trace	19·49	trace	1·78	1·50

The total is 108·76, less 8·21 oxygen, corresponding to F = 100·55. The formula of the substance is $R_2O(F,HO)_4$, and that of the pure unaltered mineral, R_2OF_4. The mineral is consequently a basic cerium fluoride which has been subjected to an incipient alteration.

B. H. B.

Meteorite at Eagle Station, Kentucky; a New Specimen of Brahinite. By S. Meunier (*Compt. rend.*, 108, 762—763).—The specimen examined was part of a meteoric mass, weighing 36·5 kilos., which was found in 1880 at Eagle Station, Carrol Co., Kentucky. Ornaments made from portions of this meteorite have been found in a prehistoric burial mound, near which it was discovered. Microscopic examination shows that the meteorite has the structure of ordinary syssiderites, and consists of a metallic paste full of vacuoles filled with stony matter. Contrary to the opinion of Kennicut, it does not resemble the meteoric iron of Atacama, but contains a notable quantity of pyroxene associated with peridote. In other words, it has the characteristics of the particular type of syssiderites which in 1870 the author distinguished by the term brahinite. The metallic paste has a concretionary structure, and contains the alloys *tænite*, Fe_6Ni, and *kamacite*, $Fe_{14}Ni$.

The only specimen of brahinite previously known was the meteoric mass found at Brahin, in Russia, in 1822. C. H. B.

Organic Chemistry.

Action of Hydriodic Acid on Allyl Iodide. By H. MALBOT (*Bull. Soc. Chim.*, **50**, 449—451; compare Abstr., 1888, 1262).—Hydriodic acid combines with allyl iodide, forming propylene iodide; on heating, this decomposes into iodine and propylene. Some of the nascent propylene unites with hydriodic acid, forming isopropyl iodide, the rest is liberated. If the decomposition is gentle, isopropyl iodide is the chief product; an energetic decomposition gives rise almost entirely to propylene.

When hydrogen iodide is passed into allyl iodide, some propylene is liberated, and great heat is evolved, eventually causing the propylene iodide which has accumulated to decompose with explosion. The explosive substance may be destroyed almost as soon as formed by alternately passing the current of acid and then warming the liquid; an explosion is thus prevented, but at the same time, the conversion of propylene iodide into isopropyl iodide is hindered, and nothing is obtained but propylene gas, and a residue of iodine, with a little carbonaceous matter. If the allyl iodide is mixed with isopropyl iodide, the reaction is much less violent, but still little, if any, allyl iodide is converted into isopropyl iodide. If, however, the mixture is cooled with ice and salt, the conversion is nearly complete.

If aqueous hydriodic acid is used, and boiled with allyl iodide in a reflux apparatus, propylene is evolved, ceasing to come off after three hours. On treating the liquid with soda, isopropyl iodide is obtained, mixed with a little propylene iodide, the volume of the product being about half that of the allyl iodide employed.

When the aqueous acid is digested with allyl iodide in the cold for 24 hours in a sealed vessel, and the liquid treated with soda, isopropyl iodide is obtained, together with some propylene.

When the experiment is performed in a sealed tube, heated for 48 hours to 100°, and the liquid washed with soda, pure isopropyl iodide is obtained boiling at 88·5°, and of sp. gr., 1·7. The propylene formed in the first part of the reaction had afterwards combined with hydriodic acid present. C. F. B.

Synthetical Formation of Formaldehyde. By K. JAHN (*Ber.*, **22**, 989).—When carbon monoxide and hydrogen are passed over spongy palladium, and then into water, the latter acquires a slight odour of aldehyde, and distinctly showed the aldehyde reaction with silver solution. The investigation will be extended to other metals and metallic oxides, &c. N. H. M.

Action of Acid Chlorides on Arsenic Trioxide. By O. POHL (*Ber.*, **22**, 973—975).—When arsenic trioxide (3·736 grams) and benzoic chloride (7·95 grams) are heated for two hours at 210°, the compound AsO_3Bz_3 is formed. This melts at about 75°, and decomposes readily into arsenic trioxide and benzoic acid when exposed to moist air. The reaction is similar to that which takes place between benzoic chloride and arsenic trisulphide.

From arsenic trioxide and acetic chloride, a compound probably of the formula AsO_3Ac_3 was obtained, but it could not be isolated, as it decomposes at the temperature required to drive off the arsenious chloride (compare Casselmann, *Annalen*, **98**, 235, and Bertrand, *Bull. Soc. Chim.*, **33**, 603, and **34**, 631). N. H. M.

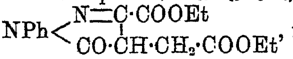
Ethyl Oxalosuccinate. By W. WISLICENUS (*Ber.*, **22**, 885—890; compare Abstr., 1888, 1273).—Ethyl oxalsuccinate,

$$COOEt{\cdot}CH(CO{\cdot}COOEt){\cdot}CH_2{\cdot}COOEt,$$

is formed when ethyl oxalate and ethyl succinate react in presence of sodium ethoxide. Sodium ethoxide (= 15 grams of sodium), free from alcohol, is covered with a layer of ether, ethyl oxalate (100 grams) is then added in small portions at a time with constant shaking, and, after remaining for several hours, the mixture is treated with ethyl succinate (119 grams), and kept for some days. The whole is then well cooled, shaken with water, the ether and unchanged ethyl succinate separated, and the solution acidified to decompose the sodium-derivative of the ethyl oxalosuccinate. The ethereal salt, which separates as a heavy, yellowish oil, is extracted with ether, the solution washed with sodium carbonate, and evaporated under diminished pressure. As the crude product (150 grams) is decomposed when distilled under diminished pressure, it is dissolved in ether, treated with a small quantity of pure potassium carbonate, the solution filtered after a short time from the flocculent precipitate which forms, and the filtrate mixed with a larger quantity of finely divided potassium carbonate. Ethyl potassio-oxalosuccinate separates in an impure state in the form of a colourless, crystalline compound readily soluble in water, and moderately soluble in alcohol; when decomposed with acids, it yields the ethereal salt in so pure a condition that it can be distilled under diminished pressure.

Ethyl oxalosuccinate is a colourless oil, boils at 155—156° (16—18 mm.), is miscible with alcohol and ether, and readily soluble in alkalis, but insoluble in water. Alcoholic solutions give a deep red coloration with ferric chloride. A solution of the sodium-derivative gives precipitates with salts of the heavy metals; the *silver-derivative* is decomposed when gently heated.

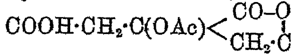
When the ethereal salt is boiled with dilute sulphuric acid, or heated at about 180° with water, it dissolves with evolution of carbonic anhydride, yielding an acid syrup which does not react with phenylhydrazine. When a dilute solution is gently warmed, it is decomposed into alcohol, oxalic acid, and succinic acid.

A compound, $C_{16}H_{18}O_5N_2$, which has probably the constitution  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}C\cdot COOEt}\\ \quad\;\; \mid \\ \mathrm{CO\cdot CH\cdot CH_2\cdot COOEt}\end{array}$, is obtained when ethyl oxalosuccinate is treated with phenylhydrazine, and the resulting *hydrazone*,

$$COOEt\cdot CH(CH_2\cdot COOEt)\cdot C(N_2HPh)\cdot COOEt,$$

heated for a long time at 150—170°, or boiled with glacial acetic acid. It crystallises from dilute alcohol in very slender needles, melts at 128—130°, and is readily soluble in alcohol, benzene, ether, and alkalis, but insoluble in water. It dissolves freely in concentrated sulphuric acid, but is reprecipitated when the solution is diluted; the alcoholic solution gives a dark violet coloration with ferric chloride. When hydrolysed with alcoholic potash, it yields an acid, $C_{12}H_{10}N_2O_5$, which crystallises from water in colourless needles containing 1 mol. H_2O, melts at 228—229°, and is insoluble in ether and benzene. The acid dissolves in sodium carbonate with evolution of carbonic anhydride, and aqueous solutions give a dark violet coloration with ferric chloride.

Ethyl oxalate (2 mols.) combines with ethyl succinate (1 mol.), yielding an ethereal salt, $C_{14}H_{18}O_9$, which melts at 89—90°, and in alcoholic solution gives a red coloration with ferric chloride. The acids obtained from this compound have peculiar reducing properties, and will be further investigated. F. S. K.

Action of Aromatic Amines on Acetylcitric Anhydride. By F. KLINGEMANN (*Ber.*, **22**, 983—987).—*Acetylcitric anhydride*,  $\mathrm{COOH\cdot CH_2\cdot C(OAc)}<\begin{array}{l}\mathrm{CO{-}O}\\ \quad\;\; \mid \\ \mathrm{CH_2\cdot CO}\end{array}$, is prepared by heating powdered citric acid, dried at 100°, with an equal weight of acetic chloride on a water-bath. The product is left to crystallise in a desiccator over soda-lime, and recrystallised from chloroform containing a little acetone, from which it separates in transparent, rhombic crystals; $a : b : c = 0{\cdot}6856 : 1 : 1{\cdot}0023$.

Citrodianilide, $COOH\cdot C_3H_5O(CO\cdot NHPh)_2$, is formed when the above anhydride is boiled in a reflux apparatus with aniline (2 mols.). The crystalline precipitate is washed with chloroform, and digested with rather strong aqueous sodium carbonate in which it almost all dissolves. The solution is filtered, precipitated with hydrochloric acid, and the acid repeatedly crystallised from alcohol. It forms white needles melting at 184°. The compound is different from that obtained by Pebal (*Annalen*, **83**, 89) by heating citric acid with aniline.

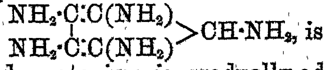
The corresponding *paratoluidide*, $C_{20}H_{22}N_2O_5$, prepared in a manner similar to the compound just described, crystallises from alcohol in small needles very like the dianilide, is insoluble in water and benzene, and melts at 161°. It is not identical with Gill's paratoluidide (Abstr., 1887, 40). N. H. M.

Organic Boron Compounds. By S. RIDEAL (*Ber.*, **22**, 992—993).—Dry ammonia reacts with boron fluoride, yielding seemingly a solid substance, BF_3,NH_3, and two liquids, $BF_3,2NH_3$ and $BF_3,3NH_3$. Boron trichloride reacts violently with aniline, with evolution of hydrogen chloride and formation of a white substance melting at 175°, insoluble in ether. Boron tribromide reacts violently with aniline and with quinoline, also with pyridine, ethylamine, dimethylamine, and trimethylamine. It seems to have no action on carbamide, oxamide, or thiocarbamide in the cold. Boron fluoride yields with aniline a white, solid substance soluble in wood-spirit but not in dry ether, light petroleum, or chloroform. N. H. M.

Oximes of Leuconic Acid and their Reduction Products. By R. NIETZKI and H. ROSEMANN (*Ber.*, **22**, 916—924).—The pentoxime of leuconic acid (compare Nietzki and Benckiser, Abstr., 1886, 449) is best prepared by gradually adding potassium croconate (30 grams) to a cooled mixture of nitric acid of sp. gr. 1·39 (45 grams) and water (40 c.c.), diluting to about 500 c.c., and, after adding hydroxylamine hydrochloride (180 grams), heating for some hours at 40—50°, and then for half a day at 100°. The precipitated oximes are dissolved in sodium carbonate, and carbonic anhydride passed through the solution (compare Nietzki and Benckiser, *loc. cit.*), whereon the pentoxime separates completely, whilst the tetroxime remains in solution, and is precipitated on adding hydrochloric acid to the filtered solution.

Leuconic acid *tetroxime*, $C_5H_6N_4O_5$, is prepared in a pure state by dissolving the tetroxime, obtained as described above, in sodium carbonate, passing carbonic anhydride to precipitate small quantities of the pentoxime, saturating the solution with sodium chloride, and purifying the sodium salt by redissolving in sodium carbonate, and reprecipitating with sodium chloride, the process being repeated several times. When the pure salt is decomposed with acids, the tetroxime is obtained as a yellow precipitate, very similar to the pentoxime. It explodes when heated to about 160°, and when warmed with aqueous hydroxylamine it is partially converted into the pentoxime. The *sodium*-derivative is very readily soluble in water, but is reprecipitated on adding alcohol or sodium chloride; the composition of the precipitate is not constant, perhaps owing to the presence of sodium chloride, but most analyses agree best with the formula $C_5H_2N_4O_5Na_2$.

The *acetyl*-derivative separates in shining plates when the pentoxime is heated at 40—50° for a long time with acetic anhydride. It is sparingly soluble in hot benzene and chloroform, separating from the latter in colourless needles containing chloroform, and from benzene in crystals which have the composition $NOH{\cdot}C_5(NOAc)_4 + H_2O$, and are decomposed when heated at 100°.

Pentamidopentene,  $\left.\begin{array}{l}NH_2{\cdot}C{:}C(NH_2)\\ \quad\ | \\ NH_2{\cdot}C{:}C(NH_2)\end{array}\right>CH{\cdot}NH_2$, is formed when finely divided leuconic acid pentoxime is gradually added to a solution of stannous chloride (1 part) and pure concentrated hydrochloric acid (2 parts), the temperature being kept below 40°, and care being taken to prevent caking; the oxime dissolves with an orange-red colour, but the solution afterwards becomes colourless. If the reaction begins to slacken, more stannous chloride solution is added; but it is not advisable to work with more than 10—15 grams of the pentoxime, and this quantity requires 100—150 grams of stannous chloride and 200—300 grams of hydrochloric acid for complete reduction. Towards the end of the operation, small quantities of the stannochloride separate in colourless needles, and on adding concentrated hydrochloric acid a further precipitation occurs. The double salt is dissolved in a small quantity of water, decomposed with hydrogen sulphide, and hydrogen chloride passed into the well-cooled solution, the temperature being kept as low as possible.

Pentamidopentene hydrochloride, $C_5H_{17}N_5OCl_4$, separates in colourless plates which are very readily soluble in water, but are reprecipitated on adding alcohol or concentrated hydrochloric acid. The aqueous solution turns brown on warming, and the dry substance is decomposed when heated at 80—100°. When dissolved in water, and the solution mixed with alcohol and ether, a compound,

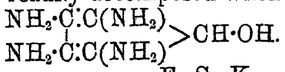
$$C_5(NH_2)_5H,3HCl + H_2O,$$

is precipitated in colourless needles which turn grey on exposure to the air.

The *sulphate*, $2C_5H_{11}N_5,5H_2SO_4 + 2H_2O$, prepared by precipitating an aqueous solution of the hydrochloride with sulphuric acid and alcohol, crystallises in small, colourless plates, and is very readily soluble in water, but only sparingly in alcohol; it is the most stable of all the salts. In aqueous solutions of the hydrochloride, platinic chloride produces no precipitate, but on evaporating, the *platinochloride* separates in large, very unstable crystals.

Pentamidopentene reacts with orthodiketones, yielding azines and quinoxalines, but the compounds are very unstable, and insoluble in all ordinary solvents. The *azine*, $C_{13}H_{13}N_5 + \frac{1}{2}H_2O$, separates in almost black needles when the pentamido-compound is treated with diacetyl and sodium acetate in aqueous solution. When an aqueous solution of the hydrochloride is mixed with a solution of potassium croconate, a compound, $C_{15}H_7N_5O_6 + H_2O$, separates in the form of an orange, crystalline precipitate; it is insoluble in all solvents, and is decomposed when heated at 100°. The salts of pentamidopentene are immediately decomposed by nitrous acid and by alkalis, but in neither case can the presence of leuconic acid in the decomposition-products be proved.

Tetramidohydroxypentene hydrochloride, $C_5H(NH_2)_4{\cdot}OH,3HCl$, is obtained in colourless crystals by reducing leuconic acid tetroxime with stannous chloride and hydrochloric acid, as described above, decomposing the resulting stannochloride with hydrogen sulphide, and passing hydrogen chloride into a very concentrated solution of the hydrochloride. The *sulphate*, $C_5H(NH_2)_4{\cdot}OH,2H_2SO_4 + H_2O$, prepared by adding sulphuric acid and alcohol to an aqueous solution of the hydrochloride, crystallises in colourless needles, and is more sparingly soluble than the hydrochloride. Tetramidohydroxypentene resembles the pentamido-derivative in its behaviour towards alkalis and nitrous acid, and, like the latter, it is readily decomposed when heated. The free base has the constitution



$$\left.\begin{array}{l} NH_2\cdot C{:}C(NH_2) \\ \quad | \\ NH_2\cdot C{:}C(NH_2) \end{array}\right> CH\cdot OH.$$

F. S. K.

Nitro-derivatives of Oxalotoluidide. By W. G. Mixter and F. Kleeberg (*Amer. Chem. J.*, **11**, 236—240).—Ladenburg obtained formorthotoluidide by heating equal parts of orthotoluidine and anhydrous oxalic acid (this Journal, 1877, 754). If, however, orthotoluidine is heated with half its weight of crystallised oxalic acid at 190°, oxalorthotoluidide is obtained. When thus prepared, oxalorthotoluidide was found to melt at 199—201°, whereas Mauthner and Suider give its melting point as 188—190° (Abstr., 1886, 886); but the authors have prepared it from orthotoluidine and ethyl oxalate, according to the prescription of these chemists, and find that this product has the same melting point and properties as their own. The yield with oxalic acid is better than with ethyl oxalate.

Tetranitro-oxalorthotoluidide, $C_2O_2[NH\cdot C_6H_2Me(NO_2)_2]_2$,

$$[Me : NH : (NO_2)_2 = 1 : 2 : 3 : 5],$$

obtained by the action of fuming nitric acid (210 c.c.) on oxalorthotoluidide (19·7 grams), crystallises from nitrobenzene on the addition of alcohol; it is white, slightly soluble in hot alcohol and glacial acetic acid, insoluble in ether and benzene, and decomposes about 270° without melting. A hexanitro-derivative was not obtained.

Tetranitro-oxaloparatoluidide, $C_2O_2[NH\cdot C_6H_2Me(NO_2)_2]_2$

$$[NH : Me : (NO_2)_2 = 4 : 1 : 2 : 6],$$

resulting from the nitration of oxaloparatoluidide by hot fuming nitric acid, forms yellow crystals, which are insoluble in ordinary solvents but soluble in warm nitrobenzene. Neither this substance nor the corresponding ortho-compound yields a dinitrotolyloxamide with potassium hydroxide.

A. G. B.

Aromatic Orthamidomercaptans. By P. Jacobson and E. Ney (*Ber.*, 22, 904—911).—Thioaceto-xylide, $C_6H_3Me_2\cdot NHCSMe$, prepared by heating aceto-xylide with phosphorus pentasulphide, melts at 94—95°; Gudeman (Abstr., 1888, 1282) gives 80° as the melting point of this compound.

Thioacetocumidide, $C_6H_2Me_3\cdot NHCSMe$, prepared in like manner, separates from alcohol in compact crystals melting at 114°.

Ethenylamidotolyl mercaptan is obtained when thiacetotoluidide is oxidised with potassium ferricyanide in dilute alkaline solution (compare Hess, Abstr., 1881, 597); it boils at 265° (corr.). The *aurochloride*, $C_9H_9NS,HAuCl_4$, is a yellowish, crystalline compound, which is decomposed when heated at about 165°.

Diamidoditolyl bisulphide, $\overset{2}{NH_2}\cdot C_6H_3\overset{5}{Me}\cdot\overset{1}{S}\cdot\overset{1}{S}\cdot C_6H_3\overset{5}{Me}\cdot\overset{2}{NH_2}$, is formed when ethenylamidotolyl mercaptan is heated at 180—190° with potash and a little alcohol, and the resulting amidotolyl mercaptan dissolved in dilute ammonia and a stream of air passed through the solution.

It crystallises in greenish-yellow needles, melts at 89°, and is readily soluble in alcohol. The *diacetyl*-derivative, $C_{18}H_{20}N_2S_2$, crystallises from alcohol in shining needles melting at 204—206°.

Ethenylamido-xylyl mercaptan, prepared by oxidising thiaceto-xylide as described above, boils at 274° (corr.). (Compare Gudeman, *loc. cit.*)

Ethenylamidocumyl mercaptan, $C_6HMe_3<\substack{N\\S}>CMe$, is prepared by oxidising thiacetocumidide with a dilute alkaline solution of potassium ferricyanide, keeping the mixture for 24 hours and digesting the precipitate with hot, dilute hydrochloric acid. The salt which crystallises from the filtered solution is decomposed with ammonia, the product, which consists of ethenylamidocumyl mercaptan and a small quantity of a compound of higher melting point, is heated at 60—65°, the liquid separated, and when cold recrystallised from dilute alcohol. It separates in colourless needles, melts at 60—62°, and is readily soluble in alcohol and ether.

Toluylene diazosulphide, $C_6H_3Me<\substack{N\\S}>N$, prepared by treating ethenylamidotolyl mercaptan with nitrous acid (compare Jacobson, this vol., p. 135), crystallises in colourless plates melting at 42—43°.

Xylylene diazosulphide, $C_6H_2Me_2<\substack{N\\S}>N$, crystallises in needles melting at 37°; *cumylene diazosulphide*, $C_6HMe_3<\substack{N\\S}>N$, separates from alcohol in prismatic crystals melting at 85°.

When the diazosulphides are heated to 200—250°, nitrogen is evolved, and diphenylene disulphide, or its homologues, are formed.

Ditoluylene bisulphide, $C_6H_3Me<\substack{S\\S}>C_6H_3Me$, melts at 116°; *dixylylene disulphide*, $C_6H_2Me_2<\substack{S\\S}>C_6H_2Me_2$, at 118°; both compounds crystallise well and dissolve in concentrated sulphuric acid with a beautiful blue coloration.

F. S. K.

Diphenylamine-derivatives. By M. Schöpff (*Ber.*, 22, 900—904).—*Hydroxydinitrodiphenylamine*, $OH\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2$, is prepared by heating orthamidophenol (10 grams) at 130—140° for five hours with dinitrobromobenzene (24 grams), distilling off the unchanged nitro-compound with steam, and after washing with dilute acid recrystallising the residue from alcohol. It crystallises in orange plates or needles, melts at 198—199°, is readily soluble in alcohol and ether, and moderately so in chloroform, but only sparingly in benzene; it dissolves in concentrated sulphuric acid with a green coloration, and in alkalis, forming a dark-red solution, from which it is precipitated on adding acids. A small quantity of a very sparingly soluble substance is formed in the above reaction; this compound is probably identical with that obtained by G. Fischer (Abstr., 1879, 924), by treating orthamidophenol with oxidising agents. The *acetyl*-derivative, $OAc\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2$, crystallises from alcohol in yellow needles, melts at 150°, and is insoluble in alkalis.

Ethoxydinitrodiphenylamine, $C_{14}H_{13}N_3O_5$, prepared by treating the hydroxy-compound with sodium ethoxide and ethyl iodide, crystallises in red needles melting at 164°. The *methoxy*-derivative, prepared by heating dinitrobromobenzene with anisidine in alcoholic solution, crystallises from alcohol in red needles melting at 151°.

Orthonitrodiphenylamine, $NHPh{\cdot}C_6H_4{\cdot}NO_2$, is prepared by heating aniline (10 grams) for 15 hours with orthochloronitrobenzene (15 grams) in alcoholic solution, separating the unchanged oils by distilling with steam, dissolving the residue in alcohol, and reprecipitating with water. It crystallises in small, lance-shaped plates melting at 75°.

Di-orthonitrophenylbenzidine,

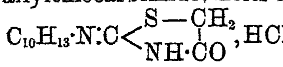
$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

is formed when benzidine, in alcoholic solution, is boiled for several hours with excess of orthochloronitrobenzene. It separates from dilute alcohol in pointed crystals and from dilute acetic acid in slender needles, melts at 240°, and dissolves in concentrated sulphuric acid with a slight red coloration, which turns dark-red on adding a trace of a nitrite. F. S. K.

Cumylamine. By H. GOLDSCHMIDT and A. GESSNER (*Ber.*, **22**, 928—933; compare Abstr., 1887, 1039).—*Diazobenzenecumylamine*, $C_6H_4Pr{\cdot}CH_2{\cdot}NH{\cdot}N_2Ph$, is prepared by gradually adding diazobenzene chloride (1 mol.) to a solution of cumylamine (2 mols.) in water containing some alcohol. The precipitate is dissolved in ether, and the residue obtained by evaporating the ether is washed with light petroleum. It forms yellowish plates, melts at 50—51°, dissolves very readily in ether, less easily in benzene and alcohol, and still less in light petroleum. The *phenylcarbamide*, $NHPh{\cdot}CO{\cdot}N(C_{10}H_{13}){\cdot}N_2Ph$, obtained as a white, crystalline mass by adding phenyl cyanate to a warm solution of diazobenzenecumylamine in light petroleum, melts at 101°. When boiled with hydrochloric acid diluted with water (2 parts), phenylcumenylcarbamide is formed.

Paradiazotoluenecumylamine, $C_6H_4Pr{\cdot}CH_2{\cdot}NH{\cdot}N_2{\cdot}C_6H_4Me$, is prepared in a manner similar to the diazobenzene-compound. It crystallises in yellowish, rhombic plates or in lustrous, stellate groups of needles, melts at 79°, and is readily soluble in ether, benzene, and alcohol, less so in light petroleum. The *phenylcarbamide*, $C_{24}H_{26}N_4O$, forms slender, white needles melting at 124°; it is decomposed by hydrochloric acid, with formation of paradiazocumylamine.

Cumylamine sulphate, $C_{10}H_{13}{\cdot}NH_2,H_2SO_4$, crystallises in plates, readily soluble in water and alcohol. The *nitrate* forms large, lustrous plates, melts at 155—157°, and is readily soluble in water and alcohol. The *cumenylcarbamate*, $C_{10}H_{13}NH_2,C_{10}H_{13}{\cdot}NH{\cdot}COOH$, is formed when cumylamine is exposed to air. It crystallises in lustrous plates melting at 97·5°. *Benzoylcumylamine*, $C_{10}H_{13}{\cdot}NHBz$, prepared from cumylamine and benzoic chloride, crystallises in lustrous plates which melt at 93°; it is readily soluble in alcohol and benzene. *Dicumenyloxamide*, $C_{10}H_{13}{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{13}$, is a white crystalline powder melting at 181—182°. Dicumenylcarbamide (Raab, this Journal, 1877, ii, 894) prepared by the action of carbonyl chloride on cumylamine dissolved in benzene, melts at 118° (not 122°). *Paratolylcumenylcarbamide*, $C_{10}H_{13}\cdot NH\cdot CO\cdot NH\cdot C_6H_4Me$, prepared by mixing ethereal solutions of cumylamine and paratolyl cyanate, crystallises from alcohol in white, matted needles of a satiny lustre, melts at 150°; it is readily soluble in alcohol, less so in ether. *Allylcumenylthiocarbamide*, $C_{10}H_{13}\cdot NH\cdot CS\cdot NH\cdot C_3H_5$, obtained from cumylamine and allylthiocarbimide, melts at 47°. *Cumenylthiohydantoïn hydrochloride*,



$$C_{10}H_{13}\cdot N:C<\begin{matrix}S-CH_2\\ |\\ NH\cdot CO\end{matrix},HCl,$$

is formed when cumenylthiocarbamide, dissolved in alcohol, is heated with chloracetic acid. It crystallises in colourless, lustrous crystals which melt at 225—235° with decomposition.

N. H. M.

Diazoamido-compounds. By H. GOLDSCHMIDT and V. BADL (*Ber.*, **22**, 933—942).—*Disdiazobenzenemethylamine*, $NMe(N_2Ph)_2$, is prepared by adding a solution of diazobenzene chloride to 33 per cent. methylamine. It crystallises in splendid, long, bright-yellow needles melting at 112—113°, and dissolves readily in ether and benzene. Boiling dilute sulphuric acid decomposes it with evolution of nitrogen and formation of methylamine, aniline, methyl alcohol, phenol, and a small quantity of amidazobenzene. When reduced with zinc-dust and acetic acid in warm alcoholic solution, methylamine and phenylhydrazine are formed.

Disparadiazotoluenemethylamine, $NMe(N_2\cdot C_7H_7)_2$, is formed, together with paradiazotoluenedimethylamine, by the action of paradiazotoluene chloride (2 mols.) on methylamine (1 mol.). It crystallises in yellow prisms, melts at 147°, and dissolves rather readily in warm ether, less in light petroleum and in alcohol. When boiled with dilute sulphuric acid, it is decomposed with evolution of nitrogen and formation of methylamine, methyl alcohol, paratoluidine and paracresol.

Paradiazotoluenedimethylamine, $NMe_2\cdot N_2\cdot C_6H_4Me$, obtained in the preparation of the above compound when ordinary but not when pure methylamine is employed, was also prepared by the action of paradiazotoluene chloride on dimethylamine. It forms colourless, rhombic plates, very readily soluble in ether and light petroleum, melts at 46°, and distils very readily with steam. Hot dilute acids decompose it into dimethylamine, paracresol, and nitrogen.

Disorthodiazoanisoïlmethylamine, $NMe(N_2\cdot C_6H_4\cdot OMe)_2$, prepared from methylamine and orthodiazoanisoïl chloride, forms groups of yellow, transparent, pointed needles melting at 140—141°.

Disparadiazoanisoïlmethylamine, $C_{15}H_{17}N_5O_2$, crystallises from ether in matted, yellow needles melting at 111—112°.

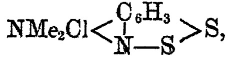
Disdiazobenzene-ethylamine, $NEt(N_2Ph)_2$, is obtained by the action of diazobenzene chloride (2 mols.) on ethylamine (3 mols.). The oily product becomes almost solid in a few days and is then crystallised from ether. It melts at 70—71°, scarcely volatilises at all with steam, and is slightly decomposed by prolonged boiling with water.

Disorthodiazoanisoïlethylamine, $NEt(N_2{\cdot}C_6H_4{\cdot}OMe)_2$, crystallises from ether in small, thick, golden prisms melting at 130°.

Disparadiazoanisoïlethylamine forms long, yellow needles melting at 114—115°.

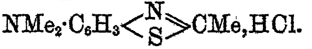
Disdiazobenzeneallylamine, $C_3H_5{\cdot}N(N_2Ph)_2$, prepared from allylamine (3 mols.) and diazobenzene chloride (2 mols.), crystallises from ether in yellow needles melting at 74°.

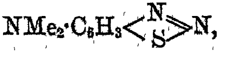
Disparadiazotolueneallylamine, $C_3H_5{\cdot}N(N_2{\cdot}C_6H_4Me)_2$, forms long, yellow, matted needles melting at 85—87°. When boiled with dilute sulphuric acid, it is decomposed into allyl alcohol, allylamine, paracresol, and paratoluidine. N. H. M.

Methylene-blue Group. By A. Bernthsen (*Annalen*, **251**, 1—97; compare Abstr., 1886, 53).—Methylene red, a bye-product in the manufacture of methylene-blue, has a constitution represented by the formula  $NMe_2Cl{<}\genfrac{}{}{0pt}{}{C_6H_3}{N{-}S}{>}S$, and is consequently a derivative of amidodimethylaniline. On reduction with zinc and hydrochloric acid, or with hydrogen sulphide, it is converted into amidodimethylaniline mercaptan. The same substance, accompanied by amidodimethylanilinethiosulphonic acid, is formed by the action of alkalis on methylene-red.

In order to prepare *amidodimethylaniline mercaptan*, the crude product of the action of zinc and hydrochloric acid on methylene-red is boiled to expel hydrogen sulphide, ammonia is added to neutralise the greater part of the free acid present, and then a concentrated solution of sodium acetate added in sufficient quantity to produce a small precipitate. The liquid is filtered, and sodium acetate added until no further precipitation takes place. The precipitated salt has the composition $Zn(C_8H_{11}N_2S)_2$. It is soluble in hydrochloric acid, strong acetic acid, and in sodium hydroxide solution. The alkaline solution absorbs oxygen, and the bisulphide is extracted from this liquid by ether. In a dilute solution of the mercaptan in hydrochloric acid, a trace of ferric chloride produces a blue coloration changing to violet-brown and finally to blue. If the solution of mercaptan contains hydrogen sulphide, ferric chloride produces a blue coloration changing to violet-brown and finally to methylene-red.

The mercaptan can also be prepared by the action of zinc-dust on alkaline or acid solutions of amidodimethylanilinethiosulphonic acid or on the acid solutions of amidodimethylaniline bisulphide. It has not been isolated. It unites with acids and alkalis. The hydrochloride is exceedingly soluble in alcohol and in water.

Acetic chloride acts on the zinc salt of mercaptan in presence of benzene, yielding the hydrochloride of *ethenylamidodimethylaniline mercaptan*,  $NMe_2{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{N}{S}{>}CMe,HCl$. This salt crystallises in slender prisms and dissolves freely in water and in alcohol. The free base is an oily liquid miscible with alcohol and ether.

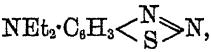
Diazothiodimethylaniline,  $NMe_2{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{N}{S}{>}N$, is formed by the action of sodium nitrite on a solution of the mercaptan zinc compound in sulphuric acid, but a much better yield is obtained from amidodimethylanilinethiosulphonic acid. The product is freely soluble in ether, alcohol, benzene, and chloroform, and melts at 78°. A solution of the diazo-compound in hydrochloric acid gives crystalline precipitates with platinic chloride, auric chloride, and potassium dichromate.

Diimidodimethylaniline bisulphide, $S_2[C_6H_3(NH_2)\cdot NMe_2]_2$, is prepared by passing air through the mercaptan zinc compound suspended in dilute ammonia. The oxidised liquid is extracted with ether, and on evaporating the extract the bisulphide remains as a thick oil, soluble in alcohol, ether, and benzene. It is also soluble in acids, but is reprecipitated from acid solutions by alkalis. The bisulphide is also formed by the action of alkalis on the thiosulphonic acid or on methylene-red, and by boiling the thiosulphonic acid with dilute sulphuric acid. A solution of the bisulphide in benzene combines with sulphur to form a persulphide, which is also obtained as a bye-product in the preparation of the bisulphide. The persulphide melts at 97° and dissolves freely in alcohol and ether. It appears to have the composition $C_{32}H_{40}N_8S_5$. A trace of the compound dissolved in hydrochloric acid gives a purple coloration with ferric chloride; this is due to the formation of methylene-red.

Amidodimethylanilinethiosulphonic acid, $NMe_2\cdot C_6H_3(NH_2)\cdot S\cdot SO_3H$, is prepared by adding an alkali to a 0·1 per cent. solution of methylene-red, until the colour of the liquid is destroyed. If a precipitate is thrown down, it must be dissolved in hydrochloric acid and the solution decolorised by alkali. The alkaline liquid is slightly acidified with acetic acid and exposed to the air in shallow vessels for 24 hours. A small quantity of ammonia is added and the mixture extracted with ether to remove the bisulphide. The liquid is feebly acidified with acetic acid, treated with charcoal, and evaporated. Paramidodimethylaniline yields a red oxidation product; this is converted into the thiosulphonic acid by the addition of a mixture of aluminium sulphate and sodium thiosulphate to the acetic acid solution. The thiosulphonic acid is also formed by the action of a strong solution of sulphurous acid on the mercaptan or bisulphide of amidodimethylaniline. It is sparingly soluble in water and alcohol, but more soluble in alkalis and in acids than in water, and melts between 193° and 204°. The dilute aqueous solution gives a purple coloration with traces of iodine or ferric chloride. The acid produces amorphous precipitates in solutions of mercuric chloride, copper sulphate, and potassium dichromate. The hydrochloride crystallises in prisms. It dissociates when brought in contact with water.

Amidodiethylanilinethiosulphonic acid, $NEt_2\cdot C_6H_3(NH_2)\cdot S\cdot SO_3H$, is most conveniently prepared by the action of potassium dichromate (3 grams) on a mixture of the zincochloride of amidodiethylaniline, $C_{10}H_{16}N_2,ZnCl_2 + 2H_2O$ (12 grams) dissolved in water (90 c.c.), aluminium sulphate (25 grams), and sodium thiosulphate (20 grams). It crystallises in slender prisms, sparingly soluble in water and alcohol, but more soluble in alkalis and acids. The potassium and sodium salts are precipitated from concentrated solutions by excess of alkali. The acid melts between 228° and 230°. It closely resembles the amidodimethylanilinesulphonic acid in all its properties, and is converted into paramidodiethylaniline mercaptan by reduction with zinc-dust and hydrochloric acid.

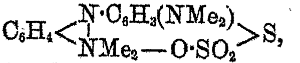
The mercaptan, $NEt_2\cdot C_6H_3(NH_2)\cdot SH$, closely resembles the corresponding dimethyl-derivative. Ferric chloride and hydrogen sulphide convert it into a red compound analogous to methylene-red. By oxidising a mixture of the mercaptan and dimethylaniline hydrochloride, diethyldimethylindamine sulphide, a soluble green dye, is produced.

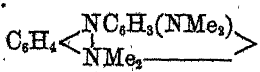
Diazothiodiethylaniline,  $NEt_2\cdot C_6H_3<{N \atop S}>N$, prepared from amidodiethylanilinethiosulphonic acid, crystallises in needles of a yellow colour, melts at 106—107°, and dissolves freely in ether, alcohol, benzene, and in acids.

Paramidodiethylaniline bisulphide, prepared by the addition of ammonium sulphide to a dilute solution of the sulphonic acid in ammonia, is a brownish-red oil. The hydrochloric acid solution gives a violet-purple coloration with ferric chloride. The picrate and thiocyanate are deposited as crystalline precipitates on the addition of picric acid or potassium thiocyanate to a solution of the hydrochloride.

Tetramethylparaphenylenediamine yields a *thiosulphonic acid*, $C_6H_3(NMe_2)_2\cdot S\cdot SO_3H$, crystallising in rhombic plates. It is soluble in hot water and in acids, and melts between 175° and 182°. This compound does not yield a green indamine. On reduction with zinc and hydrochloric acid, it is converted into the mercaptan, $C_6H_3(NMe_2)_2\cdot SH$.

Paraphenylenediaminethiosulphonic acid, $C_6H_3(NH_2)_2\cdot S\cdot SO_3H$, is soluble in hot water. The addition of dimethylaniline hydrochloride and potassium dichromate produces a bluish-green coloration which changes to blue on boiling. Reduction with zinc-dust and hydrochloric acid converts the thiosulphonic acid into the mercaptan, $C_6H_3(NH_2)_2SH$, and from this compound the bisulphide is obtained by the action of a solution of iodine. The bisulphide appears to be a yellow oil. It yields a crystalline picrate, freely soluble in alcohol.

Tetramethylindamine thiosulphonate,  $C_6H_4<{N\cdot C_6H_3(NMe_2) \atop NMe_2 - O\cdot SO_2}>S$, is prepared by oxidising a mixture of dimethylaniline and amidodimethylanilinethiosulphonic acid with potassium dichromate and acetic acid. It forms an emerald-green powder containing ½ mol. H_2O, and is termed by the author sulphonic-green or insoluble-green. On reduction it yields a leuco-compound, tetramethyldiamidodiphenylaminethiosulphonic acid, $NMe_2\cdot C_6H_4\cdot NH\cdot C_6H_3(NMe_2)\cdot S\cdot SO_3H$. This compound dissolves readily in hot alcohol and in acids. It is precipitated from the hydrochloric acid solution by sodium acetate as a white or grey flocculent deposit.

Tetramethylindamine sulphide,  $C_6H_4<{NC_6H_3(NMe_2) \atop NMe_2}>S$, obtained by oxidising a mixture of amidodimethylaniline mercaptan and dimethylaniline, is an amorphous, bluish-green powder. It dissolves in water, forming a bluish-green solution. Alkalis produce a blue precipitate in this solution. With a tannin mordant, this compound dyes calico green. When the piece is steamed, the green changes to blue owing to the conversion of the sulphide into methylene-blue. The green aqueous solution turns pale greyish-violet on the addition of hydrochloric acid, but the green colour is restored by sodium acetate. Reducing agents convert the soluble green into a leuco-compound. Tetramethylindamine sulphide is converted into the leuco-compound of methylene-blue by boiling with zinc chloride for two hours, and tetramethylindamine thiosulphonate undergoes a similar change on boiling.

Methylene-blue forms with zinc chloride a crystalline double salt, $2C_{16}H_{18}N_3SCl,ZnCl_2 + H_2O$, crystallising in copper-coloured prisms.

Diethyldimethylindamine thiosulphonate resembles the analogous tetramethyl compound.

Tetraethylindamine thiosulphonate forms green needles with a copper lustre. The sulphide is soluble in water, forming a green solution.

Dimethylindamine thiosulphonate, $C_{14}H_{15}N_3S_2O_3$, prepared by oxidising a mixture of amidodimethylaniline-mercaptan thiosulphonate and aniline hydrochloride, is an insoluble green compound. It is decomposed by hot water, probably yielding dimethylleucothionine. A green precipitate is obtained on oxidising a mixture of aniline and amidodimethylaniline mercaptan; it is converted into unsymmetrical dimethylthionine by prolonged boiling with a dilute solution of ferric chloride.

Dimethyltoluindamine thiosulphonate, $C_{15}H_{17}N_3S_2O_3$, prepared from orthotoluidine and amidodimethylaniline thiosulphonate, is a bluish-grey powder. The sulphide dissolves in water forming a bluish-green solution. On boiling it is converted into dimethyltoluthionine, a metallic green powder.

The oxidation of a mixture of dimethylaniline and paraphenylenediaminethiosulphonic acid yields a green compound, *dimethylindamine thiosulphonate*, soluble in water.

Methylene-violet is formed when potassium dichromate is added to a mixture of phenol and the zinc salt of amidodimethyl mercaptan.

W. C. W.

Derivatives of Metamidobenzamide. By W. Schulze (*Annalen*, **251**, 158—173).—Metamidobenzamide, prepared by the action of aqueous ammonium sulphide on metanitrobenzamide, melts at 78—79°, and crystallises in monoclinic prisms; $a : b : c = 0·5671 : 1 : 1·0273$; $\beta = 70° 46\frac{1}{2}'$. Dry hydrogen chloride converts it into the anhydrimide of metamidobenzoic acid, $NH_2·C_6H_4·CO·NH·CO·C_6H_4·NH_2$. This compound is decomposed by alkalis, yielding ammonia and amidobenzoic acid, and by hydrochloric acid at 200°, with the formation of amidobenzamide and amidobenzoic chloride, which decompose, yielding amidobenzoic acid.

Metadiazoamidobenzamide, $NH_2·CO·C_6H_4·N_2·NH·C_6H_4·CO·NH_2$, is prepared by passing nitrous fumes into a well-cooled alcoholic solution of metamidobenzamide. It is a yellowish, crystalline powder sparingly soluble in alcohol. The alcoholic solution gives a golden-yellow precipitate with silver nitrate. The diazo-compound interacts with phenol, yielding amidobenzamide and *metabenzamidoazophenol*,

$NH_2 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH$, the latter melts at 195° and dissolves freely in alcohol, phenol, and alkalis, forming blood-red solutions.

Diazoamidobenzamide is converted into metahydrazinebenzamide by reduction with stannous chloride or sodium sulphite. The hydrochloride, $NH_2 \cdot CO \cdot C_6H_4 \cdot N_2H_3,HCl$, is a pink powder, freely soluble in water, dilute acids, and alkalis.

Metanitrobenzoylmetamidobenzamide,

$$NH_2 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2,$$

prepared by heating amidobenzamide and nitrobenzoic chloride at 210°, is a white, crystalline powder, soluble in phenol and alcohol. It melts at 223—224°, and at 270° loses a molecule of water, and yields a compound melting at 206—207°. It dissolves in alkalis with liberation of ammonia. The addition of hydrochloric acid to the alkaline solution precipitates metanitrobenzoylmetamidobenzoic acid as a white powder, freely soluble in alcohol, phenol, and chloroform.

Metamidobenzoylmetamidobenzamide, prepared by reducing the nitro-compound with stannous chloride, forms a crystalline hydrochloride, $(C_{14}H_{13}N_3O_2)_2,HCl + 7H_2O$, soluble in hot water. The free base dissolves in 2777 parts of water at 12°, but it is freely soluble in alcohol, acetic acid, phenol, and aniline; it melts at 176°. The sulphate and nitrate are crystalline.

The *anhydrimide* of metanitrobenzoic acid,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2,$$

is prepared by heating at 200° a mixture of equivalent quantities of metanitrobenzamide and metanitrobenzoic chloride; it melts at 195°, and crystallises in pearly plates soluble in alcohol. W. C. W.

Azo-compounds of Salicaldehyde, Salicyl Alcohol, and Salicylamide. By E. TUMMELEY (*Annalen*, **251**, 174—187).—*Salicaldehydeparazobenzenesulphonic acid*, $HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot COH$, is obtained in the form of the sodium salt by shaking together a mixture of diazosulphanilic acid, salicaldehyde, and an aqueous solution of sodium hydroxide. After an interval of half an hour, the sodium salt is precipitated by the addition of acetic acid to the alkaline solution. The sodium salt forms red crystals containing 2 mols. H_2O, freely soluble in water. The free acid is prepared by adding sulphuric acid to the sodium salt, precipitating with barium carbonate, and decomposing the barium salt with sulphuric acid. The acid forms minute, red crystals, freely soluble in alcohol and water. The alcoholic solution deposits brownish-yellow plates containing 1 mol. alcohol. The acid melts at 232—235°. There are two crystalline barium salts, one $C_{13}H_8BaN_2SO_5 + 3H_2O$, is obtained by treating the free acid with barium carbonate, and the other, $C_{26}H_{18}N_2S_2O_{10}Ba + 5H_2O$, is precipitated when barium chloride is added to the free acid. The sodium salts unite with hydroxylamine to yield a crystalline *oxime*, $NaSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot CH{:}NOH$, and with phenylhydrazine to form a crystalline compound, $NaSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot CH{:}N_2HPh$. The sodium salt is decomposed by bromine, yielding diazosulphanilic acid and dibromosalicaldehyde. The dibromo-derivative melts at 85°, and is freely soluble in benzene and chloroform. It crystallises in prisms.

Salicaldehydemetazobenzenesulphonic acid, prepared from salicaldehyde and metamidobenzenesulphonic acid, forms red plates freely soluble in water and alcohol. It melts at 270°. The sodium salt containing 2 mols. H_2O and the barium salt, $C_{26}H_{18}N_2S_2O_{20}Ba + 5H_2O$, are crystalline.

Azobenzenesalicaldehyde, $Ph{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}COH$, is prepared by adding diazobenzene chloride to a concentrated solution of salicaldehyde in sodium hydroxide. An excess of alkali must be avoided. It forms yellow crystals, soluble in ether, chloroform, benzene, and hot alcohol. It melts at 128°. The sodium and lead salts and the oxime (melting at 147°) are crystalline. The phenylhydrazine compound crystallises in golden prisms and melts at 200°.

Azobenzenesalicyl alcohol, $Ph{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH$, crystallises in bronze-coloured plates and melts at 143—144°. It dissolves in alcohol, ether, and benzene. *Azobenzenesalicylamide* forms dark yellow needles soluble in ether, chloroform, and hydrocarbons, and melts at 235°. It is converted into the hydrochloride of amidosalicylic acid by reduction with stannous chloride.

Salicylamideparazobenzenesulphonic acid crystallises in pale yellow needles soluble in water, alcohol, and dilute alcohol. It unites with bases, forming crystalline salts. W. C. W.

Azo-compounds of Salicylic Acid. By L. Gebek (*Annalen*, **251**, 188—196).—*Azonitrobenzenesalicylic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}COOH,$$

prepared by the action of diazonitrobenzene chloride on an alkaline solution of salicylic acid, forms minute reddish-brown crystals, soluble in alcohol, ether, benzene, chloroform, acetic acid, and alkalis; it melts at 237° with decomposition, and yields a crystalline barium salt, $C_{26}H_{16}N_6O_{10}Ba$. The methyl salt crystallises in lemon-coloured needles which melt at 167°. *Azonitrobenzeneacetosalicylic acid* is prepared by the action of acetic anhydride on azonitrobenzenesalicylic acid at 150°; it melts at 186° and is freely soluble in alcohol, ether, and dilute alkalis. The *benzoyl*-derivative melts at 240°. Reduction with stannous chloride converts azonitrobenzenesalicylic acid into amidosalicylic acid and phenylenediamine. The acid and its hydrochloride are crystalline. A dilute alcoholic solution of azonitrobenzenesalicylic acid is reduced by potassium hydroxide and zinc-dust, yielding amidosalicylic acid and hydrazoaniline. When azonitrobenzenesalicylic acid is boiled with five times its weight of aniline, a crystalline compound of the composition $Ph{\cdot}N_2{\cdot}C_6H_3Ph{\cdot}NHPh$ is obtained. It melts at 197° and dissolves easily in alcohol and benzene.

α-Azonaphthalenesalicylic acid (P. F. Frankland, Trans., 1880, 746), prepared from α-diazonaphthalene and salicylic acid, melts at 212° with decomposition; it is soluble in alcohol, ether, benzene, and chloroform. When heated with aniline, it yields a crystalline compound, $C_{10}H_7{\cdot}N_2{\cdot}C_6H_3Ph{\cdot}NHPh$, melting at 197°. *β-Azonaphthalenesalicylic acid* crystallises in yellow needles, soluble in alcohol, ether, benzene, and acetic acid. It melts at 233°. When heated with aniline, it yields a crystalline compound soluble in benzene and melting at 236°. W. C. W.

Ethyl Bromodinitrophenylacetoacetate. By C. L. JACKSON and G. D. MOORE (*Ber.*, **22**, 990—991).—*Ethyl bromodinitrophenylacetoacetate*, $COMe\cdot CH(C_6H_2N_2O_4Br)\cdot COOEt$, is prepared by adding an alcoholic solution of ethyl sodacetoacetate (3 mols.) to tribromodinitrobenzene dissolved in dry benzene; to finish the reaction, the mixture is heated in a water-bath in a reflux apparatus for an hour. It crystallises from alcohol in yellow, rhombic plates melting at 96°. It has acid properties, and yields a deep red, readily soluble *sodium salt.* When boiled with sulphuric acid (sp. gr. = 1·44), the *ketone*, $COMe\cdot CH_2\cdot C_6H_2Br(NO_2)_2$, is obtained. This forms colourless needles melting at 113°. When the ketone is treated with aniline, a yellow, crystalline compound, $COMe\cdot CH_2\cdot C_6H_2(NHPh)(NO_2)_2$, melting at 131°, is formed, which yields a deep red, amorphous *sodium salt.*

N. H. M.

Diamidobenzophenone. By H. WICHELHAUS (*Ber.*, **22**, 988—989).—To determine whether the diamidobenzophenone prepared by the author (Abstr., 1886, 362) is identical with Städel and Sauer's compound, to which the melting point 172° was ascribed, the latter compound was prepared by Städel and Sauer's method (Abstr., 1879, 242), and found to melt at 237°; the two substances are, therefore, identical.

Diamidobenzhydrol is best obtained by dissolving diamidobenzophenone in absolute alcohol and gradually adding a slight excess of sodium amalgam. It is a white, crystalline powder, dissolves sparingly in neutral solvents, but readily in acids, and melts at 98°. α-Amidobenzophenone, the hydrol, and the sulphonic acids yield tetrazo-dyes, chiefly suitable for dyeing cotton-wool (Deut. Reichspatent, 39958, 1886).

α-Diamidobenzophenone and resorcinol yield a yellow dye, probably of the formula $CO(N_2\cdot C_6H_4)_2(C_6H_5O_2)_2$. The dye from diamidobenzophenone and α-naphthol is readily obtained in lustrous, green crystals; it dyes fibres reddish-brown. N. H. M.

Behaviour of Ketones and Aldehydes towards Sodium in presence of Indifferent Solvents. By E. BECKMANN (*Ber.*, **22**, 912—916).—When benzophenone is treated with sodium in ethereal solution, it yields a dark blue, crystalline sodium-derivative, which is very unstable in the air; this compound is converted into benzhydrol when decomposed with water, and yields a salt of benzylic acid when treated consecutively with water and carbonic anhydride.

α-Phenyl naphthyl ketone, when treated in like manner, gives *α-phenyl naphthyl carbinol*, melting at 86·5°, and *α-phenylnaphthylglycollic acid.* Benzil and benzoïn yield principally hydrobenzoïn (m. p. 135°), whether carbonic anhydride is employed or not.

Acetophenone and benzaldehyde, when treated with sodium in ethereal solution and then with water, or water and carbonic anhydride, yield chiefly pinacones, whilst acetone itself, besides pinacone, gives large quantities of products of higher boiling point.

Camphocarboxylic acid gives, under certain conditions, a crystalline oxime, melting at 160°, and the ethyl salt of this acid yields a sodium-derivative. F. S. K.

1 : 4′-Tetrahydronaphthylenediamine. By E. BAMBERGER and J. HOSKYNS-ABRAHALL (*Ber.*, **22**, 943—951; compare this vol., p. 717). —1 : 4′-*Tetrahydronaphthylenediamine*,

$$C_{10}H_{10}(NH_2)_2\ [NH_2,H:(H_2)_3:NH_2 = 1:2:3:4:4'],$$

is prepared by adding sodium (18—20 grams) in portions of 4 or 5 grams to 1 : 4′-naphthylenediamine (m. p. 189°, 14 grams) dissolved in boiling amyl alcohol (200 grams) and extracting with dilute hydrochloric acid. The acid solution is evaporated until most of the sodium chloride separates, filtered, and precipitated with soda. The base is extracted with ether, and damp carbonic anhydride passed through the solution until the base is completely precipitated as carbonate. The base is either purified as sulphate or the free base is distilled under 60 mm. pressure. It forms splendid, white crystals which gradually become coloured when exposed to air, dissolves readily in the usual organic solvents, melts at 77°, boils at 264° under 60 mm. pressure, almost without decomposition, and distils only slowly with steam. The free base gives no coloration with ferric chloride in the cold, but a deep-red colour when heated. The *carbonate* is a lustrous, crystalline powder; the *sulphate*, $C_{10}H_{14}N_2,H_2SO_4 + 2H_2O$, crystallises in thick, clear, lustrous, triclinic prisms, $a : b : c = 0{\cdot}8239 : 1 : 0{\cdot}8285$, readily soluble in water, very sparingly in ethyl or amyl alcohol. The *hydrochloride*, $C_{10}H_{14}N_2,2HCl$, crystallises in splendid, strongly refractive, rhombic prisms,

$$a : b : c = 0{\cdot}574 : 1 : 0{\cdot}906,$$

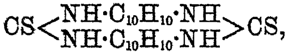
dissolves readily in water, sparingly in alcohol. The *platinochloride*, $C_{10}H_{14}N_2,H_2PtCl_6$, forms thick, orange-coloured, lustrous prisms; the *basic salt*, $C_{10}H_{14}N_2,H_2PtCl_6 + C_{10}H_{14}N_2$, is a yellow, crystalline substance readily soluble in mineral acids. The *oxalate* and *picrate* are readily soluble in water. N. H. M.

1 : 4′-Tetrahydronaphthylenediamine and α-Tetrahydronaphthylamine. By E. BAMBERGER and J. BAMMANN (*Ber.*, **22**, 951 — 968). — *Diacetyltetrahydronaphthylenediamine*, $C_{14}H_{18}N_2O_2$ [$(NHAc)_2 = 1 : 4'$], is prepared by mixing the hydrodiamine base (1 mol.) with acetic anhydride (1·5 mol.); the reaction at once takes place with explosive violence, and is finished by heating the mixture on a water-bath for an hour. It crystallises in concentrically grouped, slender prisms of a silky lustre, dissolves readily in alcohol, less in chloroform, ether, and benzene, and melts at 262°. It does not react with bromine, and dissolves in chloroform.

1 : 4′-*Tetrahydronaphthylenediamine tetrahydroamidonaphthyl thiocarbamate*, $NH_2{\cdot}C_{10}H_{10}{\cdot}NH{\cdot}CS{\cdot}SH,NH_2{\cdot}C_{10}H_{10}{\cdot}NH_2$, separates as a lustrous, crystalline powder, when an ethereal solution of the base is added by drops to a cooled ethereal solution of carbon bisulphide. It melts at 145°. The salts are rather readily soluble. It unites with diazo-compounds, yielding dyes.

Diamidotetrahydronaphthylthiocarbamide, $CS(NH{\cdot}C_{10}H_{10}{\cdot}NH_2)_2$, is formed when the compound just described is boiled with alcohol in a reflux apparatus until no more hydrogen sulphide is given off, and is purified by conversion into the sulphate. It dissolves readily in alcohol, and melts at 155°.

Diamidoditetrahydronaphthylcarbamide, $CO(NH{\cdot}C_{10}H_{10}{\cdot}NH_2)_2$, is obtained by boiling an alcoholic solution of the thiocarbamate with lead oxide until no more lead sulphide is formed. It is filtered boiling, evaporated down, and, while still hot, treated with warm water until a permanent turbidity is produced. On stirring well with a glass rod, the carbamide separates as a white, crystalline powder. It is readily soluble in alcohol, softens at 70°, and decomposes at 135° with a slight evolution of gas. Like the sulphur-derivatives, the compound has basic properties, can be diazotised, and yields dyes with diazo-compounds. The *platinochloride* and *mercurochloride* were prepared.

Ditetrahydronaphthyldithiocarbamide,  $CS{<}\begin{matrix}NH{\cdot}C_{10}H_{10}{\cdot}NH\\ NH{\cdot}C_{10}H_{10}{\cdot}NH\end{matrix}{>}CS$, is prepared by boiling the hydro-base, $C_{10}H_{14}N_2$, with an excess of carbon bisulphide in alcoholic solution in a reflux apparatus until no more hydrogen sulphide is evolved, treating with water, evaporating down, and filtering. It separates as a white, crystalline powder which dissolves readily in alcohol, and melts at 175° with evolution of gas. It reacts neutral, is insoluble in acids, and cannot be diazotised.

Tetrahydro-1 : 4′-*amidonaphthazo-β-naphthylamine*,

$$C_{20}H_{20}N_4\ [NH_2 : N_2{\cdot}C_{10}H_6{\cdot}NH_2 = 1 : 4'],$$

is prepared by adding a solution of tetrahydronaphthylenediamine hydrochloride (2 grams) and sodium nitrite (0·6 gram) to a slightly warm alcoholic solution of β-naphthylamine (1·2 gram); alcohol is added until the crystals of naphthylamine hydrochloride redissolve. Sodium acetate is then added, so that there is only a small amount of free hydrochloric acid present in the solution. After some hours, an excess of sodium acetate is added and the precipitate crystallised from alcohol. It forms orange-red prisms with a metallic lustre, dissolves readily in alcohol, sparingly in water, and melts at 262° with violent decomposition. It dissolves in strong hydrochloric acid with dark violet-carmine colour which changes to bright Bordeaux-red on diluting with water.

Tetrahydroamidonaphthol, $C_{10}H_{13}NO\ [NH_2 : OH = 1 : 4']$, is obtained when the diazo-solution prepared from tetrahydronaphthylenediamine hydrochloride (4 grams) is diluted with about an equal volume of water, treated with animal charcoal, and heated until nitrogen ceases to be evolved. The free base is a colourless oil of a sharp ammoniacal odour. It is insoluble in aqueous alkalis. It gives a deep, reddish-brown colour with ferric chloride when heated. The *hydrochloride* crystallises from water in long needles of a glassy lustre, melting at 220°; the *picrate* forms branched, lustrous needles. The *diacetyl-compound*, $C_{14}H_{17}NO_3$, forms lustrous, white needles, melts at 151—151·5°, and is readily soluble in alcohol, insoluble in acids and alkalis.

Sulphophenylazotetrahydroamidonaphthol,

$$C_{16}H_{17}N_3O_4\ [NH_2 : OH : N_2{\cdot}C_6H_4{\cdot}SO_3H = 1 : 4' : 1'],$$

is formed when the hydrochloride of the compound just described is treated with diazobenzenesulphonic acid suspended in water; after some time the dye is precipitated with a mineral acid, when it separates in lemon-coloured flakes. It crystallises from water in lustrous rosettes. The aqueous solution of the *sodium salt* has a dark Bordeaux-red colour. The solution of the *hydrochloride* has a splendid carmine colour.

Tetrahydroamidonaphthylhydrazine, $C_{10}H_{15}N_3$ $[NH_2 : N_2H_3 = 1 : 4']$, is prepared by adding a solution of stannous chloride (14 grams) in strong hydrochloric acid to a cooled diazotised solution of hydronaphthylenediamine (6 grams). The free base is a slightly brown oil which becomes thick when cooled by a freezing mixture. The *hydrochloride* crystallises in well-formed, concentrically grouped, lustrous prisms and in lozenge-shaped plates melting at 268°.

α-Tetrahydronaphthylamine, $C_{10}H_{11}{\cdot}NH_2$, is formed when a 10 per cent. solution of copper sulphate is added by drops to a solution of tetrahydroamidonaphthylhydrazine (8 grams) in water (15 to 20 parts), heated on a water-bath until the solution is coloured permanently blue. The product is treated with soda and the oil distilled in steam until the distillate is no longer alkaline. It is then acidified and evaporated down. The free base as obtained from the hydrochloride is dried with potash and then with baryta and distilled. It is a clear, viscid oil, boils at 246·5°, and dissolves in the usual organic solvents without difficulty. It resembles in its properties Bamberger and Müller's β-tetrahydronaphthylamine (Abstr., 1888, 599). It cannot be diazotised, and does not yield dyes with diazo-compounds. It gives a reddish-brown coloration with ferric chloride when heated. The *hydrochloride*, $C_{10}H_{13}N,HCl$, forms splendid, lustrous needles readily soluble in water; the *platinochloride* (with 2 mols. H_2O) crystallises in long, wide, lustrous, orange-coloured prisms melting at 190°, with evolution of gas; the *nitrite*, $C_{10}H_{13}N,HNO_2$, crystallises in splendid long, lustrous needles melting at 138—139°; it is not decomposed by boiling water. The *carbonate* and *picrate* are also described. The *acetyl-derivative*, $C_{10}H_{11}{\cdot}NHAc$, forms long prisms or hair-like needles of a silky lustre, soluble in hot water, alcohol, &c., and melts at 148—149°.

Diazobenzene-α-tetrahydronaphthylamine, $N_2Ph{\cdot}NH{\cdot}C_{10}H_{11}$, is prepared by adding crystallised diazobenzene nitrate (1 mol.) to α-tetrahydronaphthylamine (2 mols.) suspended in water, the whole being kept cold. After being kept at 0° for four to five hours, the water is poured off and the reddish-yellow oil which remains washed a few times with water, dissolved in ether, and dried with calcium chloride.

It is obtained as a syrupy oil which, when kept at a winter temperature, solidifies, forming lustrous, yellow needles. The *picrate* crystallises in long, sulphur-coloured needles of a silky lustre, dissolves readily in alcohol, rather readily in boiling water, and is insoluble in ether; it darkens at 215°, and melts with violent evolution of gas at 229—230°.

When tetrahydro-1 : 5-naphthylamine is oxidised with 3 per cent. potassium permanganate in presence of sodium carbonate, phthalic and orthocarboxyhydrocinnamic acids are formed. N. H. M.

Specific Volume of Camphor and of Borneol. By M. KUHARA (*Amer. Chem. J.*, **11**, 244—248).—The mean of the author's 11 determinations gives 0·8110 as the specific gravity of camphor at its boiling point (205·3°); the specific volume of camphor is therefore 187·42.

The specific gravity of borneol (mean of six determinations) is 0·8083 at its boiling point (209·7°); from this its specific volume is 190·5.

The calculated specific volume of camphor and borneol, taking Kopp's values for the atomic volumes of carbon (11), hydrogen (5·5) and oxygen (12·2 for ketones and 7·8 for alcohols), and regarding camphor as a ketone and borneol as an alcohol, are 210·2 and 216·8 respectively; these numbers are far different from the experimental values.

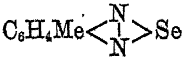
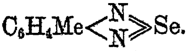
On the other hand, with Löschmidt's values ($C = 14$ for half the carbon-atoms in benzene and 11 for the other half, $H = 3·5$ and $O = 12·2$ and 7·8) the calculated specific volumes become 187·2 and 189·8 respectively, closely agreeing with the experimental values.

The author has adopted the last-mentioned values for carbon, hydrogen, and oxygen in calculating the specific volumes of other benzene-derivatives, and finds that they give results agreeing much more closely with experimental numbers than do Kopp's values.

He concludes that either Kachler's (this Journal, 1872, 1012) or Kanonnikoff's (*Ber.*, **16**, 3051) formula for camphor is correct, and that borneol is the corresponding alcohol. A. G. B.

Piaselenoles. By O. HINSBERG (*Ber.*, **22**, 862—866).—*Methylpiaselenole*, $C_7H_8N_2Se$, is obtained when selenious acid (1 mol.) is added to an aqueous solution of toluylenediamine and the mixture heated at about 80° to complete the reaction. The solution is slightly acidified with hydrochloric acid, extracted with ether, and the product recrystallised from dilute alcohol. The formation of a selenole may be employed as a very delicate test for selenious acid or for orthodiamines as, even when very small quantities (less than 1 milligram) are taken, the product can be readily identified by its smell, its very slight solubility, and by the formation of a green periodide on the addition of hydriodic acid.

Methylpiaselenole crystallises in long, colourless needles, melts at 72—73°, and boils at 267° (uncorr.), the vapours possessing a strong quinoxaline-like smell. It is readily soluble in ether and moderately so in alcohol, but only sparingly in cold water. The salts with mineral acids are yellow and are decomposed by water. The *hydrochloride* and the reddish-yellow, crystalline *platinochloride* are sparingly soluble in concentrated hydrochloric acid. Methylpiaselenole shows great similarity with the quinoxalines; it is very stable towards oxidising agents such as potassium dichromate and sulphuric acid or nitric acid, but it is readily reduced, yielding diamidotoluene and selenium, when treated with stannous chloride and hydrochloric acid or when boiled with tin and concentrated hydrochloric acid. When treated with bromine in chloroform solution, it gives a yellow, sparingly soluble perbromide which, on exposure to the air or when warmed with water, is converted into a colourless bromo-substitution product. In a solution of the base, concentrated hydriodic acid containing free iodine produces a green precipitate; this compound contains iodine, and crystallises from potassium iodide in yellowish plates, but when boiled with water for a long time it is reconverted into methylpiaselenole.

As methylpiaselenole does not react with nitrous acid or with acetic anhydride, its constitution is either  $C_6H_4Me<\overset{N}{\underset{N}{|}}>Se$ or  $C_6H_4Me<\genfrac{}{}{0pt}{}{N}{N}\gg Se$.

When a concentrated, aqueous solution of methyltoluylenediamine is treated with selenious acid (1 mol.) an intensely yellow coloration is produced, and the solution contains, in all probability, the very readily soluble *ammonium base* $C_7H_6N_2SeMe{\cdot}OH$. On adding mineral acids to the solution, yellow, readily soluble salts are formed, but hydriodic acid precipitates a *periodide* which has probably the composition $C_7H_6N_2SeMeI_3 + HI$.

Naphthapiaselenole, $C_{10}H_6N_2Se$, is obtained in brown needles when selenious acid is added to a hot, aqueous solution of α-β-naphthylenediamine sulphate and sodium acetate. It crystallises from alcohol in slightly brown needles, melts at 128—129°, and is readily soluble in ether and moderately so in alcohol, but only sparingly in water. It dissolves in concentrated sulphuric acid with an intense yellow coloration, but it is reprecipitated when the solution is largely diluted. When nitric acid is added to the solution in concentrated sulphuric acid, a yellow nitro-compound is produced. The base, like the preceding compound, is very stable towards oxidising agents, but is readily reduced and converted into naphthylenediamine.

F. S. K.

Adenine. By G. THOISS (*Zeit. physiol. Chem.*, **13**, 395—398; compare Abstr., 1885, 566, 1080; 1886, 566).—Kossel has already shown that adenine contains a hydrogen-atom which is replaceable by acid radicles. The present communication relates to the substitution of this atom by alcohol radicles. Methyl and benzyl substitution products were prepared, the latter in a pure condition; from it benzyladenine hydrochloride, sulphate, and nitrate were prepared.

Adenine and hypoxanthine contain a group, $C_5H_4N_4$, called *adenyl*. Adenin ($C_5H_4N_4NH$) is adenylimide; hypoxanthine ($C_5H_4N_4O$) is adenyl oxide. The question whether the hydrogen displaceable by benzyl is in the adenyl, or in the imide-group was investigated, and it was found that by nitrous acid benzyladenine is converted into benzylhypoxanthine. The hydrogen-atom in question is therefore contained in the adenyl-group. W. D. H.

Solution and Precipitation of Proteïds by Salts. By P. Limbourg (*Zeit. physiol. Chem.*, **13**, 450—463).—The change that fibrin undergoes when dissolved in saline solutions has been previously investigated by others (Hasebroek, Abstr., 1887, 609; Green, Abstr., 1888, 304), and the results obtained in the present research are mainly confirmatory of these former investigations; the chief proteïds that enter into solution are globulins; a certain amount of a peptone-like substance was also found; albumin is absent. Caseïn undergoes somewhat similar changes, and this takes place without the simultaneous occurrence of putrefaction. The concluding portion of the paper is devoted to showing how variable an element the heat coagulation temperature of a proteïd is, depending on the nature and strength of its saline solvent, as well as on the reaction of the solution (compare Halliburton, *J. Physiol.*, **5**). W. D. H.

Blood Pigments. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **13**, 477—496).—The red corpuscles differ from typical animal cells in their high percentage of solid constituents. Their pigment is seemingly not mixed with protoplasm, but takes the place of protoplasm. The other solids are cholesterin, lecithin, potassium phosphate, and a small quantity of proteïd. It is necessary to draw a distinction between the pigment in the corpuscles and the pigments oxyhæmoglobin and hæmoglobin separated from the corpuscles. The names *arterin* and *phlebin* are suggested for the arterial and venous pigments respectively, as contained in the corpuscles. These are probably compounds of oxyhæmoglobin and hæmoglobin respectively with lecithin. The chief differences between the corpuscular pigments and those separated from the corpuscles are:—(1.) The corpuscular pigments are insoluble; hæmoglobin and oxyhæmoglobin are soluble in the plasma and serum of the blood. (2.) The corpuscular pigments do not crystallise, give off oxygen readily in a vacuum, and decompose hydrogen peroxide readily; hæmoglobin and oxyhæmoglobin behave in all these points in the opposite manner. (3.) The arterial corpuscular pigment is not altered by a weak solution of potassium ferricyanide, whereas oxyhæmoglobin is converted into methæmoglobin.

The group which unites with respiratory oxygen is, however, the same both in the corpuscular pigment and in hæmoglobin. The spectroscopic appearances of the pigments within and without the corpuscles are also the same. That, however, is no proof that the pigments are the same inside and outside the corpuscles, because the hæmoglobins of different animals differ in percentage composition, solubility, and crystalline form, but all are alike spectroscopically. Much the same may be said for chlorophyll, which shows the typical band between B and C in the leaves, and in its decomposition-products, such as chlorophyllan and its soap. Even hæmochromogen

(Stokes' reduced hæmatin) gives a band very like that of hæmoglobin; and if the oxygen in oxyhæmoglobin be replaced by carbonic oxide or nitric oxide, the spectroscopic bands remain almost unaltered.

The carbonic oxide from CO-hæmoglobin is not displaced at the ordinary temperature, by passing a stream of hydrogen through its solutions for six hours; but at 15° the carbonic oxide is entirely displaced by this means in 1—2 hours.

If an aqueous solution of CO-hæmoglobin is heated to boiling, or to 125°, it is coagulated, but the red precipitate still shows the two typical absorption-bands. The bands also remain unaffected after treatment with dilute sulphuric acid in the cold: on heating, however, hæmatoporphyrin is formed.

If an aqueous solution of CO-hæmoglobin is heated with sodium hydroxide in the absence of oxygen, reddish-black crystals are deposited at 98—100°, which, when redissolved, show the same bands as in the original solution. These crystals consist of carbonic oxide hæmochromogen. Similar crystals of hæmochromogen are obtained by treating a solution of hæmoglobin in the same way.

The following measurements of the bands in wave-lengths were made:—

	α Band.	β Band.
Hæmochromogen	5653—5474	5269—5139
CO-hæmoglobin......	5825—5616	5505—5222
CO-hæmochromogen ..	5825—5616	5500—5222

Carbonic oxide hæmoglobin was heated with alkali in a tube in connection with a mercurial manometer, but there was no change in the tension of the gas after the decomposition had been completed. In another series of experiments, pure hæmatin was brought into contact with carbonic oxide, but no change in the volume of the gas took place: thus hæmatin does not form a compound with it; but in other cases, where the hæmatin was first converted into hæmochromogen, either by potassium hydrosulphide or sodium hydrogen sulphite, there was a diminution of the gas, corresponding with the amount absorbed to form CO-hæmochromogen. In all probability, therefore, it is hæmochromogen which, in the red corpuscles and in oxyhæmoglobin, is combined with respiratory oxygen, and in CO-hæmoglobin is combined with carbonic oxide; 1 mol. of carbonic oxide (CO) replacing one of oxygen (O_2).

The substance hæmatin can be formed by oxidising hæmochromogen; but it contains less oxygen than does oxyhæmochromogen: in the formation of hæmatin, from oxyhæmoglobin, a certain quantity of the oxygen is used up in oxidation processes. It is also regarded as probable that hæmochromogen is a ferrous compound, while hæmatin is a ferric compound. W. D. H.

Black Pigment of the Choroid. By E. HIRSCHFELD (*Zeit. physiol. Chem.*, **13**, 407—431).—Scherer (*Annalen*, **40**) was the first to investigate this pigment; this and allied pigments in melanotic sarcomata have since been examined by C. Schmidt, Dressler, Přibram

(*Chem. Centr.*, 1866, 397), Nencki (Abstr., 1888, 976), Mörner (Abstr., 1887, 168), and others.

Nencki concludes that as melanin contains sulphur and no iron, it cannot be a derivative of hæmatin, as Lehmann (*Handbuch physiol. Chem.*, 166) originally considered.

Scherer's elementary analyses are faulty, as his method of preparation of the pigment (from the eyes of oxen) left it contaminated with proteïd material; he also reckoned sulphur as oxygen.

Nencki and Sieber got rid of proteïds by digesting the pigment (which is only soluble in alkalis and concentrated mineral acids) with 10 per cent. hydrochloric acid, but their analyses from the eyes of different animals did not correspond very well.

The present research was undertaken for the purpose of ascertaining whether or not this pigment belongs to the class of humous substances (Hoppe-Seyler, this vol., p. 285; Udránzsky, Abstr., 1888, 180). No attempt was made to separate the different histological elements that contain black or brown pigment in the choroid, but the whole coat was taken, well washed with many litres of water, ether, alcohol, and 5 per cent. hydrochloric acid; the remaining pigment was dissolved by heat in 2 per cent. potassium hydroxide. From this it was reprecipitated by acid and washed as before.

The pigment so obtained contained nitrogen, but neither sulphur nor iron. Its solubilities and behaviour to reducing agents (chlorine, hydrogen peroxide, &c.) are described.

It was fused with alkali in a retort, and the distillate and residue were examined. In the distillate, the chief substance present was ammonia; only a small quantity of amines was found. In the residue, no catechol and no protocatechuic acid, but abundance of oxalic acid, and perhaps fatty acids in small quantities, were present. After fusing the pigment with alkali, the residue was insoluble in alcohol, and was free from ash. This residue has the mean percentage composition C, 65·82; H, 4·13; O, 80·05.

These facts certainly lend no support to the supposition that this pigment is related to humous substances. W. D. H.

Physiological Chemistry.

Amount of Iron in Fœtal Tissues. By G. BUNGE (*Zeit. physiol. Chem.*, **13**, 399—406).—The mineral constituents of milk are present in the same proportion as they are contained in the fœtal tissues. This is, however, not true with regard to the iron, as is illustrated by the following analysis.

100 parts by weight of ash contain:—

	In new-born dog.	In dog's milk.
K_2O	11·42	14·98
Na_2O	10·64	8·80
CaO	29·52	27·24
MgO	1·82	1·54
Fe_2O_3	0·72	0·12
P_2O_5	39·42	34·22
Cl	8·35	16·90
	101·89	103·80
Oxygen equivalent of the Cl	1·88	3·81
	100·00	100·00

The milk ash is rather richer in potash and poorer in soda than that of the new-born dog; this is easily explained by the fact that in the growing young animal, the potash-rich muscular tissue is increasing and the soda-rich cartilaginous tissue is diminishing. The higher percentage of chlorine is also explicable, as the chlorides not only serve to build up tissues, but also act largely as solvents in removing the end-products of metabolism through the kidneys. The most remarkable fact brought out by the analyses is that the percentage of iron in the milk is only one-sixth of that in the fœtal tissues. It would seem, therefore, as though the maternal organism gave to the young six times more of the other inorganic constituents than it needs. The explanation of this apparent contradiction appears to be that the fœtus obtains the greater part of its supply of iron before birth through the placental circulation. Analyses are given which illustrate the fact that a kilogram of body-weight contains less and less iron as the young animal grows. The mother has two ways in which to nourish the young: the first by the placenta, the second by the milk; the explanation that iron is given chiefly by the former is that it is the more certain, because of the difficulties of absorbing iron from the alimentary canal, and the danger that the hæmatogenous compounds may become the prey of bacteria.

It is also regarded as probable that the large quantity of iron which the mother gives to the fœtus is not all derived from the mother's food during the relatively short period of pregnancy, but that a storage of iron occurs in the maternal organs in readiness for the embryo. This begins apparently some time before the first conception, and may explain the occurrence of chlorosis at the age of puberty.

W. D. H.

Adenine, Guanine, and their Derivatives. By S. Schindler (*Zeit. physiol. Chem.*, **13**, 432—444).—In earlier quantitative estimations of nitrogenous bases in organic tissues, adenine has been partly reckoned as hypoxanthine, partly as guanine. The following method will serve for the estimation of these substances when contained in a mixture. They are dissolved in dilute hydrochloric acid; the solution is made alkaline with ammonia, and precipitated with ammoniacal silver solution. The precipitate is warmed, allowed to cool, collected, and washed with water containing ammonia. It is then treated with nitric acid and carbamide, heated on the water-bath, and filtered. To the filtrate, silver nitrate is added; it is left for 12 hours, and filtered. The precipitate is washed free from acid by cold water, then digested with hot ammonia and water; by this means the original silver oxide compounds are obtained again. To this, silver nitrate is again added, the precipitate collected and washed with water, suspended in water, and decomposed with hydrogen sulphide, and some dilute ammonium sulphide. The silver sulphide is filtered off, and the clear filtrate (*a*) contains the whole of the adenine and hypoxanthine, and part of the guanine in solution. The rest of the guanine is mixed with the precipitate, and can be dissolved out from it by hydrochloric acid, and precipitated from this solution by ammonia; this is collected, and to it is added the guanine in the filtrate (*a*), which is precipitated therefrom by digestion with ammonia on the water-bath. It is finally dried at 110° and weighed. The filtrate (*a*), freed from guanine, contains adenine and hypoxanthine, and these are weighed together after evaporation. In the mixture a nitrogen estimation is made, and the relative amounts of the two bases thus calculated. Xanthine can be estimated as xanthinate of silver.

This method gave, in a control experiment, a slight loss of guanine and adenine, and a slight gain of hypoxanthine, which is probably derived from decomposition of the adenine.

Applied to certain animal organs, the results were as follows: the numbers are percentages for the dry organs:—

	Adenine.	Hypoxanthine.	Guanine.	Xanthine.
Ox testis	none	0·281	0·177	0·222
Spermatozoa of carp .	2·278	0·309	none	0·36
Calf's thymus	1·919	0·218	0·071	0·360

The relatively high percentage (corresponding with 7·15 per cent. of the total nitrogen) in the thymus, a richly cellular organ, is especially noteworthy.

An important question is, What part do these bases play in metabolism? Kossel considers that the NH-group of adenine and guanine is replaced by O. Taking the result of putrefaction processes as an indication of what occurs within the living animal, this view was fully confirmed; adenine by the activity of putrefaction processes is changed into hypoxanthine, guanine into xanthine. In another experiment, yeast was allowed to undergo self-fermentation, and analysed at intervals with the following results:—

	Fresh yeast.	After 24 hours.	After 48 hours.	After 72 hours.
Adenine	0·1735	0·0346	traces	0
Hypoxanthine	0·3741	0·2094	0·197	0
Guanine	0·115	0·0104	0·0711	0
Xanthine........	0·0982	0·1009	0·0985	0

These numbers, however, give no definite answer as to whether or not adenine and guanine are transformed respectively into hypoxanthine and xanthine. W. D. H.

Human Bile. By S. M. COPEMAN and W. B. WINSTON (*J. Physiol.*, 10, 213—231).—The bile was obtained from a woman who suffered from obstruction of the common bile-duct due to a gall-stone. An external fistula was made by surgical means, and for some months the bile was collected and examined. Otherwise the woman was in perfect health. She died from other causes later. The case is thus a unique one, as in the few previously recorded cases where human bile has been obtained, cancer or other diseases have complicated matters.

The following is a *résumé* of the results obtained:—Calculating from the amount secreted, it is estimated that the normal amount of bile secreted by the liver is about 2½ pints per diem in a man of 12 stone. The rate of flow varies in accordance with the time of ingestion of food; there being usually a rise between one and two hours after a meal. The secretion, moreover, is not a continuous one, the bile being extruded into the gall-bladder by the repeated peristaltic contractions of the bile-ducts.

The colour of the bile in this case was always olive-green; biliverdin and not bilirubin being the pigment which was present in greatest quantity.

The quantitative estimation of the solid constituents gave the following results, which may be compared with Frerichs' analysis of normal bile:—

Constituents.	Present case.	Frerichs.
Sodium glycocholate	0·6280	9·14
Sodium taurocholate		
Cholesterin, lecithin, and fat	0·0990	1·18
Mucus	0·1725	2·98
Pigment	0·0725	
Inorganic salts	0·4510	0·78
Total solids	1·4230	14·08
Water (by difference)	98·5770	85·92
	100·0000	100·00

The low percentage of solids, especially of the bile salts, must be accounted for in the way suggested by Schiff and others, that there is normally a bile circulation going on in the body, a large quantity of the bile salts that pass into the intestine being reabsorbed and again secreted. This view is supported by the fact that cholalic acid is found in very small quantities in the fæces. Such a circulation would obviously be impossible in a case like the present.

Bile from the gall-bladder is always more concentrated than that from a fistula, probably because a portion of the water originally secreted is reabsorbed during its sojourn in the gall-bladder.

Bile is necessary for the assimilation of fats; the fæces contained in this case a large quantity of undigested fat.

Its purgative action is more than doubtful; and although it is able to a small extent to control putrefactive changes, cultivation experiments with various kinds of bacteria show that it is no true antiseptic. The bacteria grew almost as readily in the tubes containing bile as in those which did not.

In this case no bile whatever passed into the intestine, and the fæces remained uncoloured; stercobilin is therefore formed by the reduction by bile pigments in the intestine.

The urine, however, remained coloured with urobilin. Urobilin could not, therefore, have been formed from stercobilin. It is probably formed in the liver itself together with the bile pigments by a slight change of metabolism. The liver *post mortem* showed no sign of disease, and was apparently perfectly normal in function, the average amount of urea and uric acid being found in the urine.

W. D. H.

Cerebrospinal Fluid. By W. D. HALLIBURTON (*J. Physiol.*, **10**, 232—258).—The investigation deals chiefly with the following points:—

(1.) *Proteïds.*—The examination of some 16 specimens of fluid removed from cases of spina bifida and hydrocephalus entirely confirm the statement previously made on this subject (Abstr., 1887, 614) that albumoses are almost constantly present in this liquid. In two cases, true peptone (in Kühne's sense) was also found.

(2.) *Reducing Substance.*—This is not sugar, it does not undergo the alcoholic fermentation, nor rotate the plane of polarised light, nor give v. Jaksch's phenylhydrazine test. It is not glucosamine nor glycuronic acid, as its reactions do not agree with either of those substances. But it appears to be catechol; in one case this was separated in a crystalline form from the fluid. The crystals gave the characteristic reactions of catechol, but the quantity obtained was too small to admit of an elementary analysis being made.

(3.) *Salts.*—C. Schmidt made several analyses of hydrocephalus fluid, and remarked on the high percentage of potassium salts present. Subsequent investigators have not, however, confirmed this. In one case in the present research, the organic matter was destroyed by fuming nitric acid, and the salts converted into chlorides by hydrochloric acid; the ratio NaCl : KCl was found to be 95·15 : 4·85, which is about the proportion of sodium to potassium salts in blood and lymph. Ignition was only employed in this experiment to destroy the last traces of organic matter; it is when incineration is performed in the presence of a large quantity of carbonaceous matter that the danger of salts like sodium chloride being carried off is especially to be feared.

W. D. H.

The Cyst of Protopterus annectens. By G. WALTER (*Zeit. physiol. Chem.*, **13**, 464—476).—This fish lives for only three months of the year in water; during the remainder of the year it lies in the mud of dried-up rivers, and during this summer sleep is wrapped up in a cyst into an oval packet. The present investigation relates to the properties of this investing capsule.

Its ash and organic constituents were estimated and compared with those of the river mud.

The covering appears to be formed from a secretion of the mucous glands of the skin. The secretion contains mucin and inorganic salts, of which calcium carbonate is the most abundant. Small quantities of phosphoric and sulphuric acids, and alkalis were also found.

Mixed with this secretion is a certain amount of the river mud; the proportion of Fe_2O_3 and Al_2O_3 in the ash of the cyst and in the mud are approximately the same. This apparently becomes entangled with the sticky secretion and ultimately, when the river dries, incorporated with it to form the cyst. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Boric Acid as a Plant Constituent. By C. A. Crampton (*Amer. Chem. J.*, **11**, 227—232 and *Ber.*, **22**, 1072—1076).—The author has found boric acid in 34 out of 36 samples of wine from various parts of the United States, and inasmuch as Baumert has found it in wines from several European countries (this vol., p. 295) this substance must be regarded as a normal and frequently occurring constituent of the grape plant.

On extending his search for boric acid to other plants, the author has also found it in the ash of water-melons and peach trees; the ash of apples and sugar-cane gave no reaction for it; nor was it found in cider. He concludes that boric acid must be regarded as a much more general constituent of plants than has hitherto been supposed.

A. G. B.

Ash of the Indigo Stem. By J. T. White (*Chem. News*, **59**, 244).—The following are the results of the analysis of the ash from a sample of dry indigo stem, stripped of the bark, and containing 1·8 per cent. of the ash. The numbers are per cent., but less charcoal and sand or silica insoluble in sodium carbonate: CO_2, 10·56; SiO_2, 8·51; SO_3, 6·27; Fe_2O_3, 5·41; P_2O_5, 12·24; CaO, 19·36; MgO, 11·64; K_2O, 19·03; Na_2O, 4·72; NaCl, 2·26. D. A. L.

Occurrence of Lapachic Acid in Bethabarra Wood. By W. H. Greene and S. C. Hooker (*Amer. Chem. J.*, **11**, 267—270).—The wood (sawdust) was extracted with a cold 1 per cent. solution of crystallised sodium carbonate, and the red extract treated with excess of hydrochloric acid, the crystalline principle of the wood being thus precipitated; after having been freed from resin by washing with ether, it was found to possess all the properties of lapachic acid, previously described by Paternò (Abstr., 1883, 210). The yield was 0·6 per cent. of the wood. A. G. B.

Composition of Canary Seed. By A. Mayer (*Landw. Versuchs-Stat.*, 1889, 158—159).—The analysis of the seeds of *Phalaris* *canariensis* led to the following results: albuminoïds, 13·8 per cent.: fat, 5·4; extractives, 50·7; indigestible fibre, 8·2; ash, 6·8; water, 15·1. E. W. P.

Damage done to Plants by Acid Vapours. By L. JUST and H. HEINE (*Landw. Versuchs.-Stat.*, 1889, 135—158).—The authors review the work done on this subject by Stöckhardt, Nobbe, Freytag, Schröder, and others, and show by help of analyses, &c., that the appearances which plants sometimes assume and which have been generally ascribed to sulphurous anhydride from neighbouring factories, are not always due to this gas; they demonstrate that there are a variety of causes, such as temperature, moisture, fungoid growths, &c., which all tend to produce excess of sulphates and other peculiarities above referred to. E. W. P.

Note.—A paper by the Abstractor (Abstr., 1888, 744) is also criticised, but some of the criticisms are founded on an incorrect reading of the text of the original memoir. E. W. P.

Action of Water containing Sodium Chloride on Soils and Plants. By A. STOOD (*Landw. Versuchs-Stat.*, 1889, 113—118).—Water containing more than 1 gram of sodium chloride per litre damages vegetation, and even if the amount be only 0·5 gram the germination of seeds is destroyed (33 per cent.); a further action which is also detrimental to plant growth is that by reaction of zeolites, tricalcium phosphate, &c., with sodium chloride; the valuable constituents of these substances are rendered soluble and washed away out of reach of the plant, and this can occur when there is only 0·5 gram per litre. Districts, therefore, in which salt appears either in the water of irrigation or as underground or "bottom" water cannot support plants in a healthy state, for apart from the solvent action of the sodium chloride, in warm weather it is carried up by capillarity to the upper parts of the soil, becoming there concentrated and so directly inimical to life.

Analyses of soils thus affected show a large increase of sodium chloride, whilst the analyses of plants show not only increase of sodium chloride, chlorine, and total ash in the ash, but a decrease of potash and sulphuric acid. E. W. P.

Analytical Chemistry.

Volumetric Estimation of Acids. By G. LINOSSIER (*Bull. Soc. Chim.*, 50, 516).—A reply to Engel.

Alleged Reaction of Copper Salts. By A. and P. BUISINE (*Bull. Soc. Chim.*, 50, 517).—Aliamet has described (*Bull. Soc. Chim.*, 47, 754) a new reagent for detecting copper. It consists of a saturated aqueous solution of normal sodium sulphite, containing a little pyrogallol, and is said to strike a pink tint with solutions of copper, even when very dilute.

The authors state that this colour is not characteristic of copper salts, but is obtained with a solution of any metallic salt, and even with distilled water; it is not formed in an acid solution.

It is really due to the oxidation of the pyrogallol by oxygen dissolved in the solution, which is always slightly alkaline; freshly boiled solutions do not give this colour. What is really remarkable about it, is its production in presence of sulphurous acid.

C. F. B.

Detection of Chlorine, Bromine, Iodine, and Sulphur in Organic Compounds. By C. W. Marsh (*Amer. Chem. J.*, **11**, 240—244).—The author recommends that the substance be heated with finely divided zinc. In the case of solids, the operation is performed in a small sealed tube; in the case of liquids, in a test-tube, inflammable vapours being ignited and allowed to burn down the tube, thus ensuring the action of the sulphur, &c., on the zinc, some of which should be allowed to stick to the sides at the top of the tube. The halogens are detected in the residue in the tube by treating it with water and applying the usual tests; sulphur is detected by adding hydrochloric acid to the residue, and testing any evolved gas with lead acetate paper. A. G. B.

Modification of Kjeldahl's Method. By J. W. Gunning (*Zeit. anal. Chem.*, **28**, 188—191).—This modification consists in the addition of potassium sulphate (1 part to 2 parts of ordinary sulphuric acid). The potassium hydrogen sulphate formed loses water in preference to sulphuric anhydride when heated, whilst the contrary is the case with sulphuric acid alone. The organic substance is in consequence heated in contact with a stronger acid, and its oxidation is thereby greatly facilitated. About 20 or 30 c.c. is used for 1 gram of substance. The mixture is heated in a globular flask of 300 c.c. capacity, having in its neck a funnel covered with a watch-glass. The gas burner is so regulated that the greater part of the acid condenses in the upper part of the flask and flows back into the mixture. The oxidation never requires above two hours, and is frequently complete in half an hour or less. For distilling off the ammonia, the author recommends a wide condensation tube (15—20 cm.), bent at about 20 cm. from one end for connection with the flask. It should be washed out with hot acid to prevent, as far as possible, the solution of alkali from the glass by the condensing steam. The estimation of the excess of acid is most sharply effected by adding potassium iodate and iodide and titrating the liberated iodine by thiosulphate. M. J. S.

Estimation of the Total Organic Nitrogen in Water by the Kjeldahl Process. By H. Leffmann and W. Beam (*Amer. Chem. J.*, **11**, 274—277).—The authors give an abstract of Down and Martin's application of Kjeldahl's method to water analysis (*Technology Quarterly*, **2**, 3; *Chem. News*, **59**, 272). They object to the preliminary determination of the free ammonia by distilling the water, on the ground that organic matter may be destroyed by the boiling and nitrogen be lost. They recommend that the free ammonia be determined in the original water by first precipitating the calcium and magnesium with sodium carbonate and hydroxide, and then filtering and Nesslerising. To avoid the loss which is liable to occur in distilling off the ammonia resulting from the action of sulphuric acid and potassium permanganate on the water, the flask containing the green liquid, after addition of the permanganate, is heated until the green colour disappears, diluted, made alkaline with sodium hydroxide, some sodium carbonate added and allowed to settle. The clearer liquid is then filtered, and an aliquot part Nesslerised. A. G. B.

Estimation of Phosphoric Acid by Ammonium Molybdate. By F. HUNDESHAGEN (*Zeit. anal. Chem.*, **28**, 165—172). See this vol., p. 760.

Detection of Mercury in Minerals. By A. JOHNSTONE (*Chem. News*, **59**, 221—222).—To confirm the presence of mercury in a metallic sublimate obtained by heating a mineral, either with or without fusion mixture, in a tube closed at one end, two drops of strong nitric acid are added to the contents of the tube after heating, then a drop of strong solution of potassium iodide; the bottom of the tube is again heated, when the iodine volatilises and forms the characteristic red iodide with the mercury, if present. If arsenic and antimony iodides are also present, they may be destroyed by continuing the heating of the bottom of the tube gently, as the fumes of nitric acid decompose them more readily than the mercuric iodide. Another plan is to hold a small piece of gold leaf in the tube so as to catch the mercury as it volatilises, then moisten the leaf with concentrated nitric acid, and add potassium iodide; even a minute quantity of mercury will give the reaction. D. A. L.

The Electrolytic Method applied to the Separation of Mercury from Copper. By E. F. SMITH and L. K. FRANKEL (*Amer. Chem. J.*, **11**, 264—267).—Mercury can be completely separated from a solution containing a large excess of alkaline cyanide by using a comparatively feeble current (evolving 0·2 c.c. of water gas per minute). The deposit is grey, and is best washed with water. Copper under similar conditions does not deposit until all the alkaline cyanide is decomposed. Attempts to separate mercury from copper by this method resulted, in some cases, in the deposition of small quantities of copper along with the mercury, whilst in others the mercury was not entirely deposited. The errors varied from +0·05 to —0·98 per cent. of the mercury taken. The results were unsatisfactory when the copper exceeded 20 per cent. of the mercury.

Silver and copper cannot be separated by the above method.

A. G. B.

Detection of Minute Quantities of Iron in Minerals. By A. JOHNSTONE (*Chem. News*, **59**, 231).—The mineral is fused on platinum foil with potassium nitrate or chlorate, heat being applied

below, and while still warm is gradually moistened with pure concentrated nitric acid, any iron is then detected by thiocyanate.
D. A. L.

Influence of Copper on the Determination of Iron in Ferro-alloys. By T. W. HOGG (*Chem. News*, **59**, 207—208).—Both copper and organic matter, when present in a ferro-alloy, exert a reducing action during the titration of the iron with dichromate, and cause high results. To avoid this error, it is suggested to dissolve the alloy in dilute hydrochloric acid, add slight excess of potassium chlorate, boil well, reduce with sodium sulphite, expel sulphurous anhydride by boiling, and then titrate. D. A. L.

Use of Potassium Manganate in Analysis. By A. JOLLES (*Zeit. anal. Chem.*, **28**, 238—239, from *Rep. anal. Chem.*, **7**, 485).—Manganous and cobaltous salts can be titrated with potassium manganate. A measured volume of a feebly alkaline solution of the manganate, of known strength, is taken, and the manganous or cobaltous solution is added to it until the liquid is completely decolorised. The precipitates subside readily. In the case of manganese, the precipitate is pure dioxide; in the case of cobalt, it is a cobaltous manganite of the constant composition $CoMnO_3$. M. J. S.

Estimation of Tungsten in its Alloys. By J. PREUSSER (*Zeit. anal. Chem.*, **28**, 173—174).—The tedious treatment with aqua regia can be much shortened by a preliminary roasting of the finely ground alloy until it acquires a pure yellow colour. It is then dissolved in aqua regia, and the solution repeatedly evaporated to dryness with hydrochloric acid, finally drying at 120°. It is then taken up with dilute acid, and after some hours filtered. The tungstic and silicic anhydrides left on the filter are fused with sodium carbonate. The melt is dissolved in water, acidified with hydrochloric acid, and dried. The residue is treated with water, and the oxides are washed with dilute ammonium nitrate on a suction filter. They are then warmed with ammonia, which dissolves the tungstic oxide, leaving the silica. The filtered solution is evaporated and ignited; it leaves pure tungstic oxide. M. J. S.

Errors in the Assay of Fine Gold. By P. CHARPENTIER (*Compt. rend.*, **108**, 612—613).—The author has made upwards of 300 experiments with a view to determine the errors of gold assay. 0·5 gram of gold was used in each experiment, and was fused with silver and lead and afterwards treated with nitric acid in the usual way. The silver employed contained 0·24 per cent. of copper.

Too high a temperature causes a loss of from 0·0015 to 0·0035; mean 0·0024: too low a temperature, an excess of 0·0005 to 0·0008, mean 0·0006; a large excess of lead (17 grams), a loss of 0·0 to 0·0003, mean 0·0002; a very small quantity of lead (0·5 gram), an excess of 0·0004 to 0·0008, mean 0·0006; a large excess of silver (5 grams instead of 1·5), an excess of 0·0006 to 0·0015, mean 0·0010, the assay falling to powder; too little silver (0·5 gram), an excess which may equal the total weight of the gold; omission of annealing and lamination, a loss of 0·00 to 0·0025, mean 0·0008, and the assay falls to powder; conducting the first annealing at 1200°, a loss of 0·0 to 0·0010, mean 0·0003; omission of rolling, an excess of 0·0010 to a deficit of 0·0007; excessive lamination results in too energetic action of the acid and an excess of 0·0 to 0·0010, mean 0·0006; omission of the second annealing after rolling causes an excess of 0·0012 to 0·0037, mean 0·0025, and the cornet is very brilliant instead of being matt; rolling up the laminated test too tightly before treating with acid causes an excess of 0·0 to 0·0010, mean 0 0001; using nitric acid of 22° B. for all three treatments, an excess of 0·0010 to 0·0020, mean 0·0013; using acid of 32° B. for all three treatments, an excess of 0·0 to 0·0005, mean 0·0002, and the assay crumbles to pieces. The cornets should first be treated with acid of 22° B., and afterwards with acid of 32° B. C. H. B.

The Mode of Stating the Results of Wine Analyses. By J. König (*Zeit. anal. Chem.*, **28**, 202—203).—It has been recently agreed to state the results of wine analyses in grams per 100 c.c., but the author deprecates this practice, on the ground that for sweet wines, which are liable to differ widely in specific gravity, it makes the results no longer directly comparable. M. J. S.

Falsification of Oleic Acid by Linoleic Acid. By Granval and Valser (*J. Pharm.* [5], **19**, 232—236).—Oleic acid is much used in the woollen manufacture, and the presence of linoleic acid causes serious inconvenience. In testing for this adulterant, comparative experiments should be made on commercial oleic acid of good quality. (1.) The impure acid has a yellowish-brown tint, paler than the standard. (2.) The density is higher, say 0·912—0·919 in various samples at 15°, whilst the standard never exceeds 0·905. As the impure sample is clotty at 15°, it is necessary to take the specific gravity at a higher temperature and add 0·00064 for each degree above 15°. (3.) On heating the impure acid to 50°, it becomes more consistent after cooling, and this change is accentuated each time the operation is repeated up to a certain point. (4.) 50 grams dissolved in 450 c.c. of 85 per cent. alcohol produces on shaking a glistening precipitate, whilst pure oleic acid dissolves completely; other oils give deposits, but not of the same character. The precipitate is collected, washed with alcohol, dried, and is then found to melt at about 47°. It is easily saponified, yielding a soda soap completely soluble in water, with which it forms a jelly on cooling when only present to the amount of 1 : 100. (5.) If Poutet's reagent be applied to the impure acid, the mass remains more or less liquid, whilst oleic acid becomes solid by the following day. (6.) A thin film of the impure acid soon becomes resin-like, whilst the oleic remains almost unchanged. (7.) If a few drops of impure acid are added to soda-lye, an intense yellow colour is produced, whilst the pure acid gives a greyish tint only.

J. T.

Free Fatty Acids in Oils. By H. Noerdlinger (*Zeit. anal. Chem.*, **28**, 183—187).—The determinations were made by dissolving

	A.			B.			C.		
	Min.	Max.	Mean.	Min.	Max.	Mean.	Min.	Max.	Mean.
Rape-seed oil	0·53	1·82	1·19	0·52	6·26	2·88	0·77	1·10	0·93
Olive oil	—	—	1·66	3·87	27·16	12·97	—	—	—
Poppy oil	0·70	2·86	1·92	12·87	17·73	15·37	2·15	9·43	4·72
Earth-nut oil	0·85	3·91	1·94	3·58	10·61	6·52	0·95	8·85	4·02
Oil of sesame	0·47	5·75	1·97	7·17	33·13	17·94	2·62	9·71	4·89
Cotton-seed oil	—	—	0·15	0·42	0·50	0·46	—	—	—
Oil of mustard	—	—	—	0·68	1·02	0·85	—	—	—
Castor oil	—	—	—	0·62	18·61	9·28	1·18	5·52	2·78
Linseed oil	—	—	—	0·41	4·19	1·57	—	—	—
Candle-nut oil (seed of *Aleurites moluccana*)	—	—	—	—	—	56·45	—	—	—
Palm-kernel oil	—	—	—	3·3	17·65	6·91	4·17	11·42	8·49
Palm oil (old)	—	—	—	—	—	50·82	—	—	—
Cocoanut oil	—	—	—	3·03	14·35	7·92	1·00	6·31	4·26
Ilippe fat (3 years old)	—	—	—	—	—	28·54	—	—	—
Niam fat (from the fruit of *Lophira alata*)	—	—	—	—	—	..	14·40	34·72	24·56
Bicuhyba fat (3 years old)	—	—	—	—	—	18·55	—	—	—
Japan wax	—	—	—	—	—	9·25	—	—	—

the oils in a mixture of ether and alcohol, adding phenolphthaleïn, and titrating with N/10 potash. The free acid is calculated as oleic.

The samples examined were of three kinds (see table, p. 800):—

A, table oils obtained by pressing.
B, expressed commercial oils.
C, oils extracted by light petroleum in the laboratory.

They were all fresh except where otherwise stated.

The percentage of fatty acid is largely influenced by the ripeness of the fruit and the conditions under which it has ripened. There is no characteristic percentage for any oil. For table oils, the presence of between 1 and 2 per cent. of free fatty acid appears advantageous as regards flavour. M. J. S.

Butter Analysis. By L. F. Nilson (*Zeit. anal. Chem.*, **28**, 175—183).—The author's mode of conducting Reichert's process, which has been officially adopted in Sweden, is minutely described. The 2·5 grams of fat (obtained in the case of a milk analysis by evaporating the ethereal solution of Soxhlet's areometric fat determination) is saponified in a 200 c.c. flask by 5 c.c. of alcoholic potash (20 grams of potash to 100 c.c. of 70 per cent. alcohol), heating directly over a gas flame, so that most of the alcohol is expelled. It is essential to remove the last traces, which is done by heating the flask in boiling water whilst drawing air through it with the water-pump, until on closing the inlet the soap no longer intumesces in the partial vacuum. The soap is then dissolved in 50 c.c. of water, and distilled with 20 c.c. of a 20 per cent. solution of orthophosphoric acid, heating by a flame which is so regulated that 1 c.c. distils per minute. When 50 c.c. has condensed, the operation is stopped. The distillate is filtered, and the insoluble fatty acids washed with 50 c.c. of hot ammonia-free water; it is then titrated with N/10 potash. With care in the various operations, the differences between duplicate determinations will rarely amount to 0·1 c.c. of potash. The whole of the volatile acid is not contained in the first 50 c.c., but the amount obtainable by further distillation appears very constant. It is suggested that it is due to the presence of small quantities of lauric acid.

From the examination of 843 samples of butter-fat from 15 cows, the following conclusions are drawn:—The extreme limits in the volume of potash consumed by normal milk are 20·5 and 11·45 c.c. Out of 797 cases there were only 44 which fell below Reichert's 12·5 limit. The fat of colostrum is poorer, requiring 9 to 10 c.c. The amount rapidly rises to a maximum in 5—7 days, and then slowly and regularly falls during the whole period of lactation, uninfluenced by season or ordinary changes in food. Individuals, however, differ greatly. Rutting, or illness immediately after calving, causes marked depression in the proportion of volatile acids. M. J. S.

Specific Gravity of some Fats and Oils. By C. A. Crampton (*Amer. Chem. J.*, 11, 232—236).—The author gives a table of the specific gravity, at various temperatures, of lards and of fats and oils used in compounding commercial lards, as determined by him with the specific gravity flask. The table also gives the coefficient of expansion, and the specific gravity as calculated from this, of the said lards, fats, and oils. A. G. B.

Colour-reactions of some Ethereal Oils. By A. IHL (*Chem. Zeit.*, 13, 264).—Oil of peppermint, when mixed with alcohol and finely-powdered beet-sugar, gives a moderately intense bluish-green colour on heating with hydrochloric or dilute sulphuric acid, neither menthol nor oil of mint give this reaction.

Alcoholic phloroglucinol and concentrated hydrochloric acid give a bright red coloration with oil of cloves, a deep dark red with oil of cassia, and an intense rose-red with pimento-oil. Resorcinol, in a similar manner, gives respectively red-violet, cinnabar-red, or dirty violet; pyrogallol, with oil of cloves, a violet colour. All three oils give a yellow colour with alcoholic aniline sulphate and hydrochloric or dilute sulphuric acid, and orange with α-naphthylamine.

These reactions are identical with those of lignin, and are, therefore, possibly due to the eugenol present in the oils. D. A. L.

Quantitative Estimation of Nicotine. By M. POPOVICI (*Zeit. physiol. Chem.*, **13**, 445—449).—Nicotine is extracted from the tobacco by Kissling's method, and then estimated by the polarimeter. The specific rotatory power of nicotine is $[\alpha]_D = 161{\cdot}55°$. In an alkaline solution it rotates the ray to the left, in an acid solution to the right. The results obtained are a little higher than by Kissling's titration method. W. D. H.

Separation and Estimation of Adenine, Guanine, and their Derivatives. By S. SCHINDLER (*Zeit. physiol. Chem.*, **13**, 432—444). See p. 790.

Analysis of Cinchonas. By E. LANDRIN (*Compt. rend.*, **108**, 750—753).—The experiments were made with *Cinchona* (*quinquina*) *succirubra*, which is cultivated in Java by the Dutch Government.

300 grams of the finely-powdered bark is mixed with 75 grams of calcium oxide suspended in water, and 75 grams of a solution of sodium hydroxide of 40° B. The use of both alkalis is essential to complete extraction of the alkaloïds, 2 litres of petroleum is then added and the mixture heated at 100° for about 20 minutes with continual agitation. The petroleum is decanted off, and the residue treated in a similar manner with a second quantity of 2 litres. The 4 litres of oil is then agitated for 10 minutes with 75 c.c. of a 10 per cent. solution of sulphuric acid and 150 c.c. of water, the acid liquid decanted off, and the treatment repeated with the same quantities, and a second time with half the quantities. The first and second acid solutions are heated to boiling and neutralised with ammonia, in order to precipitate the resins, and the third acid liquid, which is used to wash the filter in the first operation, is treated in a similar manner. When the neutralised liquids cool, they deposit, in the form of sulphates, about 90 per cent. of the alkaloïds present in the bark. The mother-

liquors are precipitated with sodium hydroxide, and the precipitate is treated with just sufficient dilute sulphuric acid to convert it into sulphate. The sulphates are weighed together and the different alkaloïds separated in the usual way. The *Cinchona succirubra* examined contained:—Total alkaloïds 7·592 per cent.; crystallisable salts, 5·183 per cent.; quinine sulphate, 2·127 per cent.

Water dissolves from the bark the greater part of the acid principles which it contains; alcohol is about equally efficient, but, contrary to the usual statement, it was found that dilute hydrochloric acid dissolves a slightly smaller quantity. C. H. B.

Evaluation of Ipecacuanha. By A. LYONS (*Zeit. anal. Chem.*, **28**, 258—259, from *Amer. J. Pharm.*).—10 grams of the powdered root is digested for 24 hours with 40 c.c. of water in a warm place, and then further for three days after making up to 100 c.c. with alcohol. 25 c.c. of the clear liquid is then acidified with sulphuric acid and warmed until the alcohol is expelled. It is again made up to 25 c.c. with water, and titrated with Mayer's potassio-mercuric iodide reagent, of which 1 c.c. = 0·0189 gram of emetine. Flückiger (*Pharm. Zeit.*, **31**, 30) extracts 10—20 grams of ipecacuanha powder in a Soxhlet's apparatus with chloroform to which 1 c.c. of liquid ammonia has been added, distils off the chloroform, and weighs the emetine after drying at 100°. Lyons finds 1·65 to 3 per cent., Flückiger only 1 per cent. of emetine in the root. M. J. S.

Examination of Commercial Peptones. By J. KÖNIG and W. KISCH (*Zeit. anal. Chem.*, **28**, 191—201).—The methods hitherto in use for estimating the soluble and non-coagulable proteïds (the albuminoses and peptones) are far from satisfactory. The precipitation of the albuminoses by ferric acetate, with subsequent precipitation of the peptones by sodium phosphotungstate, yields very discordant results. The authors adopt the method of Kühne and Chittenden, precipitation of the albuminoses with a saturated solution of ammonium sulphate, and in another portion the precipitation of both albuminose and peptone by sodium phosphotungstate, and estimation of the peptone from the difference. From 5 to 20 grams of substance (according to the proportion of water it contains) is taken. The insoluble matter and coagulable albumin are separated by filtration and by boiling, and their amount determined. This is preferably effected by Kjeldahl's nitrogen process. Multiplication of the nitrogen found by 6·25 gives the amount of albumin more correctly than direct weighing. The filtrate is made up to 500 c.c.: of this 50 c.c. or 100 c.c. is evaporated to about 10 c.c., and mixed with 100 c.c. of a saturated solution of ammonium sulphate in the cold. The precipitate is filtered off, washed with ammonium sulphate solution, dried, and weighed, and the ammonium sulphate adhering is ascertained by a sulphuric acid determination and deducted. Of the same filtrate 50 c.c. or 100 c.c. is acidified with sulphuric acid, and precipitated with a strongly acid solution of sodium phosphotungstate. The precipitate is washed with dilute sulphuric acid, and the nitrogen it contains is determined. Although albuminose and peptone contain less nitrogen than albumin, the same multiplier should be used, as this will to some extent compensate for the traces of other nitrogenous substances precipitated at the same time.

Salkowski (*Berlin. Klin. Wochensch.*, 1885, No. 2) gives the following differences between albumin-peptone, gelatin, and gelatin-peptone (a $3\frac{1}{2}$—5 per cent. solution being used).

	Albumin-peptone.	Gelatin.	Gelatin-peptone.
5 vols. of glacial acetic acid and 5 vols. of sulphuric acid mixed.	violet	yellowish	yellowish.
An equal volume of concentrated sulphuric acid in the cold.	dark-brown	yellow	yellow.
Millon's reagent	reddish pp.	colourless	colourless.
Solution boiled with $\frac{1}{5}$ vol. of nitric acid (1·2), then made alkaline with soda.	deep orange	lemon-yellow	lemon-yellow.

M. J. S.

General and Physical Chemistry.

Dispersion in Organic Compounds. By P. BARBIER and L. ROUX (*Compt. rend.*, **108**, 1249—1251).—The authors adopt as a measure of dispersive power the value of the coefficient B in Cauchy's formula $n = A + \frac{B}{\lambda^2}$, and in order to calculate the values of A and B they measured the indices of refraction of two lines in the spectrum of tin, $\lambda = 6452$ and $\lambda = 4524$ respectively.

	T.	n_r.	n_b.	A.	B.
Benzene	10·5°	1 4974	1·5221	1·4735	0·9967 × 10^{14}
Toluene..................	10·2	1·4917	1·5152	1·4690	0·9483 „
Ethylbenzene	10·4	1·4927	1·5151	1·4719	0·9039 „
Isopropylbenzene	10·1	1·4888	1·5102	1·4681	0·8636 „
Isobutylbenzene...........	10·1	1·4905	1·5110	1·4707	0·8272 „
Isoamylbenzene	10·3	1·4887	1·5084	1·4717	0·7950 „

The value of A remains constant, but the value of B diminishes as the molecular weight increases. The relation between the dispersive power and the molecular weight is represented by the formula $y = \alpha + \beta x + \gamma x$, in which y = the dispersive power, and x the molecular weight; $\alpha = +1340·5$, $\beta = -5·21$, $\gamma = +0·0103$. The values calculated by means of these constants agree almost absolutely with the actual determinations. Moreover, in the hydrocarbons derived from benzene by a single substitution, the dispersive powers are inversely proportional to the cube roots of the molecular volumes.

Examination of other benzene-derivatives not hydrocarbons gave the following results:—

	T.	n_r.	n_b.	A.	B.
Benzyl alcohol............	16·9°	1·5365	1·5618	1·5120	1·0209 × 10^{-14}
Monochlorbenzene..........	13·8	1·5213	1·5466	1·4968	1·0209 „
Acetophenone	16·1	1·5128	1 5385	1·4879	1·0371 „
Monobromobenzene	13·9	1·5555	1·5837	1·5282	1·1380 „
Phenyl cyanide	16·1	1·5236	1·5519	1·4962	1·1420 „
Benzaldehyde	15·7	1·5400	1·5742	1 5069	1·3801 „
Aniline	15·2	1·5798	1·6168	1·5440	1 4931 „
Nitrobenzene..............	14·0	1·5442	1·5841	1·5055	1·6101 „

C. E. B.

Relation between Potential Difference and Striking Distance in Atmospheric Air, Hydrogen, and Carbonic Anhydride at Different Pressures. By F. PASCHEN (*Ann. Phys. Chem.* [2], **37**, 69—96).—Baille (*Ann. Chim. Phys.* [5], **29**, 187), in his experiments on the potential difference required to cause a spark to pass in atmospheric air at different pressures, arrived at the conclusion that between the pressures of 25 and 125 cm. of mercury the potential difference required to give a spark of given length was proportional to the pressure.

Macfarlane (*Phil. Mag.* [5], **10**, 389) made a number of experiments at lower pressure, and came to the conclusion that the relation between the potential difference and the pressure for a given length of spark could be expressed by means of a hyperbola. The results obtained by the author agree fairly well with those of Baille for comparatively low pressures, but not so well at higher pressures. His results do not agree so well with those of Macfarlane, but this may very possibly be due, as the author suggests, to the fact that Macfarlane's experiments having been made in a glass vessel, the electrification of the vessel would necessarily introduce an error the amount of which could not be estimated with any approach to accuracy. The author finds that the curves expressing the potential difference in a given gas as a function of the pressure for a given striking distance, and as a function of the striking distance for a given pressure respectively, are of a similar character. The curves in both cases are approximately hyperbolic, and do not differ very greatly from straight lines.

The observations show that in a given gas the potential difference required to produce a discharge depends only on the product of the density of the gas into the shortest distance between the electrodes, so that this potential difference, and therefore what Maxwell calls the *electric strength* of the dielectric, depends only on the number, and not on the mean distance of its molecules. In other words, the striking difference at a given potential difference is proportional to the mean length of path of the molecules of the dielectric.

The author's experiments were all made at a constant temperature of about 20°, but Cardani (*Rend. Accad. dei Lincei*, **6**, 44) has shown that the potential difference required for a given length of spark remains unchanged when the gas is heated even as high as 3000°, so that the electric strength of a gas is independent of the relative velocity of its molecules, and depends only on their number.

The author finds that in the case of carbonic anhydride the potential difference required to produce a spark of given length, and also the electrostatic force, are considerably greater than for air and for hydrogen, provided the sparking distance is small.

He also finds that, for a given value of the product of pressure into striking distance, the potential difference required to produce a spark is not so constant in carbonic anhydride as in the other two gases, but slightly increases as the striking distance is diminished. This result appears to afford a strong confirmation of the hypothesis adopted by Maxwell to explain the relatively high values of the electrostatic forces at very small distances between the electrodes, namely, that the layers of gas are condensed on the surfaces of the electrodes, and that when the distance separating them is small, these layers touch each other, so that the density of the gas between the electrodes, and therefore its electric strength, would be considerably greater than would be concluded from the observed pressure in the vessel containing the electrodes; for carbonic anhydride, like all easily condensible gases, forms a much denser layer upon smooth surfaces than gases like atmospheric air or hydrogen.

G. W. T.

Dropping Electrodes. By W. OSTWALD (*Zeit. physikal. Chem.*, **3**, 354—358).—A reply to Exner and Tuma (this vol., p. 456), in which the author defends his former results, as being in agreement with those obtained from observation of the maximum surface-tension, and calls in question the statement that chemical action and polarisation take place.

H. C.

Electrical Resistance of Bismuth. By E. v. AUBEL (*Compt. rend.*, **108**, 1102—1104; compare Abstr., 1888, 545).—Metallic bismuth obtained by the reduction of the oxychloride prepared from ordinary commercial bismuth or from the basic nitrate used by Marignac for the determination of the atomic weight, was found by spectroscopic analysis to contain traces of lead. Although the lead was only detected with difficulty even in this way, it exerts very considerable influence on the electrical resistance of the bismuth, and measurement of the resistance is the most sensitive of all tests for the presence of lead in bismuth.

Pure bismuth perfectly free from lead was obtained by electrolysis of a solution of the commercial metal, the bismuth being deposited on the cathode, and lead peroxide on the anode. Part of this bismuth was fused and cooled gradually, whilst the remainder was fused and cooled quickly or tempered.

After the first heating, the metal undergoes permanent modification, and the resistance acquires a constant value. Leduc has previously observed an analogous phenomenon. The same bismuth cooled slowly or rapidly has the same properties, the resistance being practically the same, and hence it seems that the molecular changes resulting from the mode of cooling have practically no effect on the electrical properties of electrolytic bismuth, although they exert a great effect in the case of the ordinary impure metal.

With slowly cooled bars of both pure and impure bismuth, the variation of the resistance with temperature is positive, but the presence of traces of lead increases the resistance at 0°, whilst it reduces the coefficient of variation. Unlike all other forms of the metal, the coefficient of variation of electrolytic bismuth is constant between 0° and 100°.

The divergences between the results of physicists who have investigated the properties of bismuth are explained by the extreme rarity of the pure metal.

The specific resistance of bismuth in c.g.s. units at 0° is $107\cdot99 \times 10^8$ if slowly cooled, and $108\cdot69 \times 10^8$ if cooled rapidly. The coefficient of variation with the temperature between 0° and 100° is +0·00429 if slowly cooled, and +0·00422 if quickly cooled.

The author has also measured the variation of the resistance in a magnetic field of approximately 1560 c.g.s. units. If R is the resistance out of the magnetic field, and ΔR the variation in the field, then with bismuth which has been slowly cooled the quantity $100 \frac{\Delta R}{R}$ is 2·9 at 0° and 0·415 at 99·7°. C. H. B.

Electrical Conductivity of Saline Solutions. By P. CHROUSTCHOFF (*Compt. rend.*, **108**, 1003—1006).—The author has determined by Bouty's method the electrical conductivity of a number of simple salts, and expresses the results in terms of the conductivity of a solution of potassium chloride of the same concentration. Mixtures of salts of the same acid were treated in a similar manner. In the case of potassium sulphate and sulphuric acid, the results agree with those calculated from the results of Berthelot's thermochemical investigation of the composition of the solutions. C. H. B.

Electrical Conductivity of Saline Solutions; Reciprocal Displacement of Acids. By P. CHROUSTCHOFF (*Compt. rend.*, **108**, 1100—1102).—This is a continuation of the author's previous researches, and the conductivities are expressed in terms of the conductivity of a solution of potassium chloride of the same degree of concentration. Acetic acid is completely displaced by hydrochloric acid, and the results agree with thermochemical data, whereas the values calculated from the avidities differ to a much greater extent from the experimental numbers. In the case of potassium nitrate and hydrochloric acid, the results are in agreement with thermochemical data and not with the avidity formulæ.

Sulphuric acid displaces tartaric acid almost completely, although partition of the base between the two acids takes place to a slight extent, a result which agrees with Berthelot's conclusions, whilst the values calculated from avidity formulæ show wide deviations. In the case of acetic and tartaric acids, the base is divided between the two acids. Berthelot found that in solutions much more dilute than those used by the author, tartaric acid displaces acetic acid completely. When sodium acetate is mixed with oxalic acid, there is likewise a division of the base between the acids.

In the case of potassium sulphate and hydrochloric acid, the observed conductivity agrees with the calculated mean conductivity of the system, a result which does not conform to any of the usual views respecting the constitution of this mixture. It is evident, however, that the system $K_2SO_4 + 2HCl$ will be more stable under conditions which tend to prevent the formation of potassium hydrogen sulphate. Moreover the conductivity is increased by the presence of free hydrochloric acid. It is, therefore, to be expected that in dilute solutions the conductivity will approach the mean conductivity of the two inverse systems, and will even exceed the lower of these in the case of salts of the heavy metals, which are more easily decomposed by water.

These views are completely confirmed by the results of the author's experiments, all of which are given in the form of a table.

C. H. B.

Electrical Conductivity of Saline Solutions. By P. Chroustchoff (*Compt. rend.*, **108**, 1161—1162).—The methods already described were applied to mixtures of different salts in equivalent proportions. The conclusions arrived at are as follows: (1) Starting with any system of two salts, the same conductivity is obtained as with the inverse system; (2) the conductivity of the mixture is not the mean conductivity of either system of two salts, nor is it intermediate between the two mean conductivities, but is generally lower than either. This points to a reduction in the number of conducting molecules in the liquid, or, in other words, to the formation of double salts. The typical reaction as represented by the ordinary equation for double decomposition is rarely met with, and in almost all cases the change is complicated by secondary reactions. C. H. B.

Electrical Conductivity of Saline Solutions. By P. Chroustchoff and V. Pachkoff (*Compt. rend.*, **108**, 1162—1164).—The results described in this paper were obtained with mixtures of two salts which were not likely to interact. The conductivity of each solution was determined separately, and they were then mixed in equivalent proportions. In some cases the observed conductivity of the mixture is the mean conductivity of its constituents; in other cases it is lower. It follows that with the degree of dilution employed there is a reduction in the number of conducting molecules, either by formation of double salts, as with some of the sulphates, or by dissociation by the water, as in the case of zinc acetate. It is noteworthy that, as a rule, mixtures of salts which crystallise with water have the mean conductivity of their constituents, whilst the conductivity of mixtures of salts which form anhydrous crystals is below the mean.

C. H. B.

Conductivity of Solutions of Zinc Sulphate containing Gelatin. By C. Lüdeking (*Ann. Phys. Chem.* [2], **37**, 172—176).—Wiedemann has shown (*Ann. Phys. Chem.*, [2], **20**, 537) that in the case of aqueous solutions of zinc sulphate containing glycerol, there is no proportionality between the frictional resistance and the electrical resistance. At Wiedemann's suggestion the author determined to make a similar series of experiments with gelatin in the place of glycerol.

The author finds (1) that when the temperature is varied, there is no sudden change in the conductivity as the gelatin passes from the solid to the liquid state. (2) The change in conductivity with the temperature increases with the proportion of gelatin in the solution, a result in contradiction to that obtained by Arrhenius, who arrived at the conclusion that the temperature coefficient of the conductivity was independent of the proportion of gelatin.

The author attributes the difference in the results obtained by himself and Arrhenius respectively to the fact that the latter experimented only with solutions containing a very small proportion of gelatin. He finds that the effect of an increase in the proportion of gelatin in the solution becomes less as the proportion of zinc sulphate is increased. G. W. T.

Loss of Voltaic Energy of Electrolytes by Chemical Union. By G. Gore (*Phil. Mag.* [5], **27**, 353—359).—A continuation of the author's researches on the amount of dissolved salts required to disturb the voltaic balance (compare this vol., p. 665). The amount of free chlorine required (for an astatic galvanometer of 100 ohms resistance) is 1 part in 1,282,000,000, of potassium chloride 1 in 699,803, of potassium chlorate 1 in 239. These numbers represent the fall in voltaic energy of chlorine, as it is combined successively with potassium and oxygen. In this research, the action of a further addition of salts is examined. It is found that each new salt added occasions a fall in voltaic energy. Thus potassium chloride added to potassium chlorate in equivalent proportion reduces the energy to 53. If to this mixture ammonium oxalate be added in the proportion represented by $KClO_3,KCl,Am_2C_2O_4$, the energy falls to 28·4. A similar fall with increased complexity occurs with other mixtures of salts, and there appears to be no limit to the reduction of voltaic energy in this way. With a mixture having the composition

$$Na_2SO_4,K_2SO_4,2NaCl,2KCl,K_2CrO_4,$$

the voltaic energy is a negative quantity. That is to say, the electromotive force of a zinc-platinum couple with such an electrolyte is less than that of one with pure water. With mixtures which give negative quantities, the largest negative value is obtained when the constituents are in equivalent proportions. H. K. T.

Heat of Formation of Alkaline Carbonates in very Dilute Solution. By J. A. Muller (*Ann. Chim. Phys.*, **15**, 517—533).—If the heat evolved in the neutralisation of an alkali and of an alkaline carbonate or an alkaline hydrogen carbonate by one and the same acid, such as hydrochloric acid, is determined under the same conditions of temperature and dilution, the heat of formation of the carbonate or hydrogen carbonate under the same conditions is equal to the difference between the heat of neutralisation of the alkali and that of the carbonate or hydrogen carbonate. The author has previously determined the heat of formation of carbonates and hydrogen carbonates of the alkalis and of some amines (Abstr., 1885, 716, 1038); in the present paper the experiments are repeated, but with this difference, that the solutions employed were so dilute that the whole of the liberated carbonic anhydride remains in solution.

The heat evolved when a solution of an alkali or carbonate is poured into aqueous solutions of carbonic anhydride was also determined; the solutions employed contained 0·3—0·5 mol. excess of carbonic anhydride, but it was proved by preliminary experiments that this excess has no appreciable effect on the results.

As a rule, after mixing the acid with the alkaline solution the temperatures of the mixtures attained equilibrium in 1—1½ minutes; the mixture of hydrochloric acid and amylamine hydrogen carbonate, however, required 2 minutes, and when dilute solutions of carbonic anhydride are mixed with solutions of amylamine carbonate 3 minutes elapse before the maximum temperature is reached.

If the heat of dilution of the hydrochloric acid, which in these experiments amounted to 0·47 Cal. for 2 mols. of the acid, is subtracted from the heat evolved in neutralising with hydrochloric acid, the difference gives the heat of neutralisation of the alkali or alkaline carbonates in solutions infinitely dilute; in the same way, if the heat of dilution of the alkali or alkaline carbonate solutions is subtracted from the heat evolved by the combination of the dissolved carbonic anhydride with the alkali or carbonate, the difference gives the heat of combination in solutions infinitely dilute.

The following table, compiled from the experimental data, which are given in full, shows the heat evolved (in Cals.) in the neutralisation of alkalis by hydrochloric acid and carbonic anhydride in very dilute solutions.

Alkalis (2 mols.).	Hydrochlorides or chlorides.	Normal carbonates.		Hydrogen carbonates.	
	$A-0{\cdot}47$.	$A_2-a_2-A_1+a_1$.	$A-A'$.	A_2-a_2.	$A-A''$.
Methylamine	25 90	16·61	16·85	19·40	19·78
Dimethylamine	23·98	15·25	15·45	18·29	17·84
Trimethylamine......	17·86	8·00	8·00	11·61	11·97
Tetramethylammonium hydrate....	27·92	21·03	20·41	22·46	21·94
Isoamylamine........	27·11	17·03	16·51	21·28	20·93
Lithia..............	28·17	—	20·41	—	22·11
Potash..............	27·86	20·20*	20·35	22·00*	21·99
Soda	27·97	20·50*	20·53	22 20*	22·02

A, A′ and A″ = the heats of neutralisation of the alkali, carbonate and hydrogen carbonate respectively with hydrochloric acid. A_2 and A_1 = the heats of neutralisation of the alkali and carbonate respectively with carbonic anhydride; a_2 and a_1 = the heats of dilution of the alkali and alkaline carbonate solutions respectively. F. S. K.

Heat of Combustion of Carbon. By BERTHELOT and PETIT (*Compt. rend.*, **108**, 1144—1148).—Finely powdered wood charcoal was treated successively with boiling hydrochloric and hydrofluoric acids, heated to bright redness in a current of chlorine, and then heated in a Perrot's furnace. It contained 99·34 per cent. of carbon and 0·66 per cent. of ash. Six determinations were made in the calorimetric bomb with oxygen under a pressure of 25 atmos.

Crystallised graphite was purified by successive treatments with hydrochloric acid, washed, dried, and heated to redness for a short time in presence of air. In order to burn the graphite, it was mixed with one-third to one-fifth of its weight of naphthalene, the heat of combustion of which is accurately known. Five determinations were made.

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* Berthelot, *Essai de Mécanique chimique.*

Powdered Cape diamonds containing 0·12 per cent. of ash were mixed with 11 to 16 per cent. of their weight of naphthalene. Four determinations were made. Two other determinations with *bort* gave practically the same result.

Heat of combustion.	Charcoal.	Graphite.	Diamond.
1 gram	8137·4	7901·2	7859·0

$$\begin{aligned}
&\text{C (diamond)} + O_2 = CO_2 \text{ develops } +94{\cdot}31 \text{ Cal.}\\
&\text{C (graphite)} + O_2 = CO_2 \quad ,, \quad +94{\cdot}81 \quad ,,\\
&\text{C (charcoal)} + O_2 = CO_2 \quad ,, \quad +97{\cdot}65 \quad ,,
\end{aligned}$$

C. H. B.

Heats of Combustion and Formation of Nitriles. By Berthelot and Petit (*Compt. rend.*, **108**, 1217—1222).—The combustions were made in the calorimetric bomb. The following table gives (1) the heat of combustion at constant pressure; (2) the heat of formation from its elements, carbon being in the form of diamond; (3) the heat of transformation into the solid ammonium salt of the corresponding acid by assimilation of water:—

	(1.)		(2.)	(3.)
(Formonitrile)	152·3	138·3	−23·5 Cal.	+13·3 Cal.
Acetonitrile	291·6		+0·5 ,,	+12·5 ,,
Propionitrile	446·7	155·1	+8·7	+8·8 ,,
Benzonitrile	865·9	164·8	−33·1	+20·4 ,,
Orthotolnic nitrile ...	1030·7		−27·9 ,,	—
Benzyl cyanide	1023·8		−34·8	
Oxalic nitrile........	262·5	132·6	−73·9	+68·7
Malonic nitrile.......	395·1		−43·2	+53·5
Succinic nitrile	546·1	151·0	−32·0	+49·2
Glutaric nitrile	699 8	153·7	−22·8	—

The conversion of benzyl cyanide into the isomeric orthotoluic nitrile develops + 6·9 Cal. As a rule the heats of formation of the nitrites are negative, a fact which explains their tendency to undergo change. Hydration results in considerable development of heat, especially in the case of nitriles of bibasic acids, a fact of considerable importance in physiological chemistry. In homologous series the increase is from 8 to 10 Cal., except in the case of the first two members, where the difference is nearly three times as great as between any other consecutive pair. C. H. B.

Determination of the Specific Gravity of Salts which are Soluble in Water. By J. W. Retgers (*Zeit. physikal. Chem.*, **3**, 289—315).—It is pointed out that great discrepancies usually exist in the results given by various observers for the specific gravity of a salt which is soluble in water, few of these agreeing even to the second decimal place. This is mainly due to the great difficulty in obtaining perfectly pure and homogeneous crystals of a soluble salt with which to work. Examined under the microscope, it is seen that most crystals contain cavities enclosing mother-liquor, air or other impurities. Such crystals are, however, invariably lighter than those which are free from impurity, and hence a separation can be effected. For if the salt be thrown into a liquid of about its own specific gravity, the crystals which first sink are those which are the purest, and if the liquid be a mixture, its specific gravity can be so adjusted that only the pure crystals will sink, the impure floating on the surface, and thus the two will be separated. Further, as the crystals which just sink are of the same specific gravity as the liquid, a measurement of the specific gravity of this liquid will at once give that of the pure salt.

The author discusses at length the relative merits of various methods for putting the above into practice. He finds a mixture of methylene iodide (sp. gr. 3·3) with benzene to be the most useful liquid to employ. The following are the results with the salts examined, and are correct to within one unit of the third decimal place:—

	t.	Sp. gr.		*t.*	Sp. gr.
K_2SO_4	20°	2·666	KCl	16°	1·989
$(NH_4)_2SO_4$	20	1·774	KNO_3	16	2·109
$MgSO_4,7H_2O$	16	1·678	$NaNO_3$	15	2·265
$FeSO_4,7H_2O$.....	15	1·899	$K_2SO_4,Al_2(SO_4)_3,24H_2O$	17	1·751
$CuSO_4,5H_2O$	16	2·286	$Tl_2SO_4,Al_2(SO_4)_3,24H_2O$	15	2·318
NaCl	17	2·167	—	—	—

H. C.

The Density Numbers of Groshans. By G. T. GERLACH (*Zeit. anal. Chem.*, **28**, 290—314).—This paper consists in great part of an account of the main facts of the law of density numbers compiled from the scattered publications of Groshans, as well as from private communications received from him by the author. The present Abstract is supplementary to those that have already appeared (1886, *passim*).

1. *Boiling Points.*—The absolute boiling points of compounds are related to their density numbers, so that for a group of substances $\frac{TB}{M} = k$, a constant (Abstr., 1886, 194). The number of these constants is indefinite. In homologous series they increase regularly, being of the form $27·8 \sqrt{\frac{q}{2}} + y$, where q is the number of hydrogen-atoms in the molecule, and y is zero or some small integer. In the ethers of the fatty series $y = 0$, in the isomeric alcohols and acids $y = 3$.

2. *Latent Heats of Vaporisation.*—L_h being the latent heat of

vaporisation of 1 gram of a substance, it is connected with the density numbers by the expression—

$$L_1 = \frac{27\cdot8 \times 21\cdot139}{B} \sqrt{x}.$$

For many substances, as for instance the compound ethers, $x = \frac{q}{2} + y$.

3. *Heat of Combustion.*—The heat of combustion of 1 gram of a substance $= \frac{33x}{B}$. The value of x varies in different series. For the paraffins it is $\frac{q}{2}$; for the alcohols $\frac{q}{2} - 1$; for the fatty acids $\frac{q}{2} - 2$.

4. *Specific Gravity of Solutions.*—The density numbers of many of the elements are most readily obtained from the properties of their compounds in a state of solution. The difference between the molecular volume of a solution and the volume of the solvent, termed by Thomsen the "residue" (r), tends to diminish to a constant as the solution is progressively diluted. The maximum value of r is approximately equal to the molecular volume of the dissolved compound. The minimum value is such that for similar compounds of two analogous elements the differences $(r - r')$ are constant. Thus $(K - Na)Cl = (K - Na)NO_3$. Now, Groshans shows that the specific gravity (d) of any aqueous solution may be expressed by

$$d = 1 + \frac{B\gamma/3 - M}{A + M},$$

where B equals the density number of the compound, A the number of molecules of water used for dissolving 1 mol. of the salt, M a small number which is constant for a great many substances of similar constitution, and $\gamma = \frac{a + 18M - r}{6B}$ (a being the molecular weight): γ always has a value between 1·2 and 1·27, the average being 1·23. For the haloïd salts of monatomic and diatomic metals $M = 1$. The density number of sodium chloride (for which the minimum value of r is 16) is, therefore, obtained from $\frac{58\cdot5 + 18 - 16}{6 \times 1\cdot26} = 8$, and since that of chlorine is 4 (deduced from that of hydrochloric acid), that of sodium is also 4. When unit molecules of salts having the same density number, and for which the values of M are equal, are dissolved, each in the same number of molecules of water, their solutions will have the same specific gravity. Such solutions are termed "isobaric." In the case of isobaric substances $a - a' = r - r'$.

A possible connection between the molecular weights and the density numbers exists in the fact that in many cases groups of allied elements whose molecular weights differ by 45 (approximately) have density numbers differing by 5, whilst, in at least some instances, differences of molecular weight of 2 or 3 times 45 correspond with differences of density numbers of 2 or 3 times 5 respectively.

The author points out that the unqualified statement of Groshans, as to the equality of the specific gravity of solutions of isobaric salts, is applicable only to solutions of high dilution. At the same time much remains to be learnt respecting the expansion of salt solutions with rise of temperature, as also the proper temperature for making comparisons of specific gravity, especially as the practice of referring specific gravities to the weight of an equal volume of water at the same temperature, although the expansion of the solutions is usually different from that of water, may well introduce confusion into the results. M. J. S.

Dissociation of Saline Hydrates and Analogous Compounds. By H. Lescœur (*Ann. Chim. Phys.*, **16**, 378—403).—The results obtained by Wiedemann (this Journal, 1874, 946, 1131), Naumann (*ibid.*, 1875, 426), and Precht and Kraut (*Annalen*, **178**, 129) in their experiments on the dissociation of saline hydrates, cannot be depended on, as sufficient care was not observed in excluding all traces of air and moisture. Parreau's apparatus (*Ann. Phys. Chem.* [2], **1**, 55) only allows of experimenting within a limited range of temperature, and Müller-Erzbach's measurements of the rapidity of dissociation (*ibid.*, **23**, 607, and **24**, 409) give no absolute or relative indication of the tension of dissociation. The rapidity of dissociation is not only a function of the tension of dissociation, but depends also on the physical state of the substance. The rate of evaporation of water itself is not comparable to the rapidity of dissociation of solid hydrates. (Compare Schulze, *Ann. Phys. Chem.*, **32**, 329.)

The author describes with the aid of diagrams two methods for determining the tension of dissociation of saline hydrates.

The apparatus employed in the first method consists of a graduated barometer-tube (A), 1 metre in length and 15—20 mm. in diameter, placed perpendicularly in a mercury-trough and surrounded, just as in Hofmann's vapour-density apparatus, by a larger glass tube through which the heating vapour circulates. A smaller, semi-capillary tube (B), bent at right angles, is passed to within a short distance of the upper extremity of A, and serves as a support for a small tube containing the salt to be examined. The shorter limb of B projects through the side of the mercury-trough, and is in connection with an air-pump; it is provided with a three-way stopcock immersed in the mercury. The substance having been placed in position, the barometer-tube (A) is exhausted; the three-way cock is then turned so that the mercury ascends in B, and A is brought to a constant temperature by means of some suitable vapour. The first depression of the mercury column never shows the true vapour-tension owing to the presence of air contained in the crystals and hygroscopic water; the first observations are, therefore, neglected and the tube is again exhausted and then closed as before. The depression now observed, after making all the necessary corrections, shows the true vapour-tension, and by exhausting the apparatus from time to time the substance can be further dissociated and the various tensions measured.

The salt is finally analysed. When the tensions to be measured approach 760 mm. the surface of the mercury becomes cooled by conduction and may condense some of the aqueous vapour. In order to overcome this difficulty, the end of the barometer-tube (A) is closed with a cork (through which B passes), the mercury-trough is done away with, and the three-way cock in B is replaced by a simple one. A lateral tubulus, close to the lower extremity of the barometer-tube (A), connects the latter by means of stout, india-rubber tubing with a graduated burette-shaped tube (E) placed parallel to the barometer-tube, and provided at its lower extremity with a three-way stopcock; by this means, the level of the mercury in A and E can be regulated at will.

In the second method described by the author, the salt is placed in a large, wide-mouthed flask which is closed with a cork pierced with two holes, through one of which passes a thermometer, through the other a small, polished metal tube; the latter contains ether and a very delicate thermometer. The whole apparatus having attained a constant temperature, a stream of air is passed through the ether and the dew-point is observed. The maximum tension of aqueous vapour at this temperature is then ascertained from Regnault's tables. The apparatus gives very good results, except when the tension to be measured is considerably less than the maximum tension of water-vapour at the same temperature. The results are not trustworthy when the temperature of the surrounding medium is more than 20° higher than the dew-point, or if the readings are taken before the temperature of the interior of the flask has become perfectly constant. In ascertaining the dew-point the metal tube should be cooled as quickly as possible, or else the temperature of the air in the flask is lowered and the readings are inaccurate. F. S. K.

The Absorption of Carbonic Anhydride by Mixtures of Alcohol and Water. By O. MÜLLER (*Ann. Phys. Chem.* [2], **37**, 24—43).—The author points out that, although a large number of investigators have taken up the subject of absorptive phenomena, the only one who has experimented on the absorption of mixed liquids is Setschenoff, who has investigated the question of the absorption of carbonic acid by mixtures of sulphuric acid and water (*Bull. Acad. St. Pétersbourg*, **22**, 102).

In the present paper, the author describes the results of an investigation, taken up at the suggestion of Wiedemann, of the absorptive powers of mixtures of alcohol and water for carbonic anhydride. The results obtained, when compared with those given by Setschenoff, exhibit some very interesting analogies between the behaviour of dilute sulphuric acid and that of dilute alcohol.

In the case of alcohol the coefficient of absorption diminishes as the proportion of alcohol increases, and reaches a minimum when the solution contains 28 per cent. of alcohol, after which it continues to increase up to the value for absolute alcohol. When the solution contains about 45 per cent. of alcohol the value of the coefficient of absorption is about the same as for pure water. In the case of sulphuric acid the variation of the coefficient of absorption is represented by a curve of similar character, the minimum being attained when the proportions are such as to give the first hydrate of sulphuric acid, $H_2SO_4 + H_2O$. The curve showing the deviation of the coefficient of absorption from the mean of its values for water and alcohol respectively is also found to be of the same character as the similar curve showing the deviation of the coefficient of absorption of dilute sulphuric acid from the mean of the values for water and pure acid respectively.

In both cases the coefficient has two maxima and two minima, and the maxima correspond, as in the case of alcohol, to the proportions giving the chemical compounds $C_2H_5{\cdot}OH + 6H_2O$ and $C_2H_5{\cdot}OH + 3H_2O$. In the case of sulphuric acid the proportions are those which give the compounds $H_2SO_4 + H_2O$ and $H_2SO_4 + 2H_2O$. In addition to these similarities the minimum value of the absorption-coefficient corresponds in both cases with the maximum value of the heat of mixture, occurring when the composition of the solution is represented by $C_2H_5{\cdot}OH + 6H_2O$ and $H_2SO_4 + H_2O$ respectively.

The greatest diminution of volume occurs when the proportions correspond to the composition represented by $C_2H_5{\cdot}OH + 3H_2O$ and $H_2SO_4 + 2H_2O$ respectively. G. W. T.

Crystallisation and Physical Union. By G. BRÜGELMANN (*Ber.*, **22**, 1052—1053; compare *Ber.*, **17**, 2359).—The real crystalline form of any chemical compound is that which it assumes when in a pure condition.

The author's views on mixed crystallisation, which have been previously stated (*loc. cit.*), cannot be proved experimentally, as there are no methods by which the absolute simultaneousness of crystallisation of two or more compounds can be determined. F. S. K.

Diffusion in Agar Jelly. By F. VOIGTLÄNDER (*Zeit. physikal. Chem.*, **3**, 316—335).—Graham has shown that diffusion takes place in many colloid substances, as in water, and the author finds this to be the case with a jelly made from agar-agar. Such a jelly containing 1 per cent. of agar is specially adapted for studying diffusion, as it can be made to take and retain any desirable form, and the progress of salts or acids through the mass can be indicated by colour changes. The salt can be allowed to diffuse from an aqueous solution into the jelly, as the process is in no way disturbed by any interchange of water between the two.

In this way the author has been able to prove the truth of Fick's law of diffusion for dilute solutions, and finds that the diffusion constants are equal to those found in aqueous solution in some cases and greater or less than these latter in others. The rate of diffusion of a substance is the same for solutions of agar of different concentration. The diffusion constants do not change with rise of temperature, but the amount of diffused salt regularly increases.

H. C.

Chemical Action between Solids. By W. HALLOCK (*Amer. J. Sci.*, **37**, 402—406).—Ice when brought into contact with such solid salts as are used in producing freezing mixtures, for instance, the chlorides of sodium, potassium, ammonium and calcium, potassium nitrate, or sodium and potassium hydroxides, combines with them to form aqueous solutions, provided that the temperature, although even far below the melting point of either the ice or the salt, is higher than that of the resulting solution. The author is led to infer that the formation of alloys by pressure (Abstr., 1888, 1163) may be due to the combining metals forming freezing mixtures, and finds in fact that the combination of sodium and potassium takes place with absorption of heat.

From the readiness with which potassium and sodium act on dry ice, it also appears probable that in such an apparent action between solids the aqueous vapour surrounding the ice initiates the action, and it can be shown that similar occurrences take place in other cases of so-called chemical action between solids. It seems, however, that even though the reagents are solid, chemical action may take place wherever the product or products are liquid or gaseous. H. C.

Constants of Affinity of Organic Acids, and their Relations to Composition and Constitution. By W. OSTWALD (*Zeit. physikal. Chem.*, 3, 170—197, 241—288, and 369—422).—The author has shown in a former paper (Abstr., 1888, 1142) that by the aid of the theory of the dissociation of electrolytes the conductivity, and hence also the chemical activity of an acid can be fully represented by an expression containing only one constant, which is dependent on the nature of the acid itself. This constant c is equal to $(1 - m)v/m^2$, where m is the molecular conductivity for the solution diluted to v litres in terms of the conductivity for infinite dilution. If we set $\gamma = c/2$, then $(1 - m)v/m^2 = 2\gamma$, where the constant γ depends solely on the nature of the acid, and when $m = \frac{1}{2}$, $v = \gamma$, that is γ will also represent the dilution for which the dissolved substance is one-half dissociated. With strong acids, γ will have a very small value; with feeble acids, it will become very great indeed.

Although the latter method of representation makes the physical meaning of the constant very evident, the great differences in the values for feeble and strong acids render its use in this form objectionable, and the author therefore substitutes for it $k = 1/2\gamma = m^2/(1 - m)v$, this being then a direct measure of the activity or amount of dissociation of the acid in solution. k is for the most part constant with rising dilution, but in some cases the value decreases, this being most probably due to the substance being slightly impure.

The author has determined the values of k for a large number of organic acids, and has established many important relations with regard to its dependence on composition and constitution. The substitution of any negative radicle for hydrogen in the acid always increases its value, the increase being the greater the nearer the substituent is to the carboxyl-group of the acid. This is shown by the following examples:—

Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$	k = 0·00134
Lactic acid, $CH_3{\cdot}CH(OH){\cdot}COOH$	0·0138
Hydracrylic acid, $CH_2(OH){\cdot}CH_2{\cdot}COOH$....	0·00311
Benzoic acid, $C_6H_5{\cdot}COOH$................	0·0060
Orthochlorbenzoic acid, $C_6H_4Cl{\cdot}COOH$	0·1320
Metachlorbenzoic acid, $C_6H_4Cl{\cdot}COOH$......	0·0155
Parachlorbenzoic acid, $C_6H_4Cl{\cdot}COOH$......	0·0093

The differences in the values of k according to the position which a negative radicle occupies in the molecule are as a rule so great as to serve at once to distinguish and characterise isomerides. It is also possible to predict the values of k for certain compounds by the study of those of other related compounds, and hence also to determine the composition and constitution of acids from this single property. H. C.

Reversible Transformation of Copper Potassium Chloride. By W. Meyerhoffer (*Zeit. physikal. Chem.*, **3**, 336—346).—When the double chloride of copper and potassium, $CuCl_2,2KCl,2H_2O$, crystallising in blue plates, is heated either alone or in presence of a desiccating agent, such as acetic acid, brown needles are formed of the composition $CuCl_2,KCl$. The reaction which takes place, $CuCl_2,2KCl,2H_2O = CuCl_2,KCl + KCl + 2H_2O$, is a reversible one, and the temperature at which the transformation occurs is found to be about 92°. If a mixture of the above salt with cupric chloride be taken, the reaction is slightly different: $CuCl_2,2KCl,2H_2O + CuCl_2,2H_2O = 2CuCl_2,KCl + 4H_2O$, but in this case also is reversible, the temperature of transformation being about 55°. In each case the decomposition is attended with a large increase in volume, and hence the exact temperature of the change is easily ascertained by means of a dilatometer. H. C.

Unit of Atomic Weights. By W. Ostwald (*Ber.*, **22**, 1021—1024).—The author argues in favour of making oxygen the standard of the atomic weights of all other elements, as it is from oxygen that the atomic weights are actually determined. (Compare Meyer and Seubert, this vol., p. 753.) F. S. K.

Basis of Atomic Weights. By B. Brauner (*Ber.*, **22**, 1186—1192).—A reply to Meyer and Seubert (this vol., p. 753), in which the author points out that the ratio H : O = 1 : 15·96, determined by Regnault, is attended with experimental errors, that Erdmann and Marchand's experiments gave 1 : 16, and Dumas', as has been shown by Ostwald, 1 : 15·98 as the lowest limit. As, therefore, no value of the ratio H : O between 1 : 15·87 and 1 : 16·01 has been proved to be accurate, least of all the value 1 : 15·96, O = 16 should be taken as the standard of atomic weights. F. S. K.

Unit of Atomic Weights. By L. Meyer and K. Seubert (*Ber.*, **22**, 1392—1396).—A reply to Ostwald.

Molecular Determinations from Osmotic Pressure. By A. LADENBURG (*Ber.*, **22**, 1225—1226).—The proof of the applicability of Avogadro's law to dilute solutions (compare van't Hoff (Abstr., 1888, 778) has rendered it possible to determine the molecular weight of substances in solution by ascertaining the osmotic pressure. The author is working out a method by which this principle can be employed for chemical purposes, but as the apparatus, in its present form, does not give accurate results, the details are not given. Molecular weight determinations with grape-sugar, resorcinol, cane-sugar, and benzoicsulphinide gave results within 8—10 per cent. of the true value. It is also intended to employ this method for estimating the water of crystallisation of substances in solution.

F. S. K.

Estimation of the Molecular Weights of Dissolved Substances. By W. WILL and G. BREDIG (*Ber.*, **22**, 1084—1092).—The authors propose to use a modification of Tamman's (Abstr., 1888, 403) and Walker's (this vol., p. 6) methods for estimating the vapour-tension of a solution, in order to measure the influence of the substance in solution on the vapour-tension of its solvent, and to use the results so obtained to determine the molecular weight of the dissolved substance. The solution is contained in a specially constructed Liebig's bulb (*a*) having a large number of bulbs, and the pure solvent in another similar bulb (*b*). These bulbs are weighed, joined together, and then air passed through for about 24 hours at the rate of about a litre per hour, the two bulbs being kept immersed in a bath of constant temperature. At the end of the operation the bulbs are again weighed. The loss in weight of *a* is proportional to the vapour-tension of the solution, that of *b* to the difference of the vapour-tensions of the pure solvent and of the solution. From these figures the molecular weight of the dissolved substance may be calculated by Raoult's formula—

$$M = m : \frac{p}{100} \cdot \frac{f'}{f - f'},$$

where

M is the mol. wt. of the dissolved substance.
m is the mol. wt. of the solvent (for alcohol = 46).
p is the number of grams of substance dissolved in 100 grams of the solvent.
f is the vapour-tension of the solvent } at equal temperatures.
f' " " solution } at equal temperatures.

If s' be the loss of weight of the bulbs containing the solution, s'' that of those containing the solvent—

$$\frac{f'}{f - f'} = \frac{s'}{s''},$$

and substituting this in the first equation—

$$M = m \cdot \frac{p}{100} \cdot \frac{s'}{s''}.$$

The authors have tried a number of solvents, but find alcohol the best: the formula then becomes—

$$M = \frac{46 \,.\, p \,.\, s'}{100\, s''}.$$

The following are the results obtained in a number of trials, the number in brackets immediately following the name being the true atomic weight. Nitrobenzene (123), 122, and 127; acetamide (59), 58; ethyl benzoate (150), 137, and 143; benzoic acid (122), 107, and 108; picric acid (229), 264; diphenylamine (169), 153, and 146; atropine (289), 275, and 250; hyoscyamine (289), 263; formamide (45), 49, and 50; ethyl salicylate (166), 187, and 189; urethane (89), 87, and 91; carbamide (60), 60, and 61; vanillin (152), 130, and 135; and acetovanillon,* $OH{\cdot}C_6H_3(OMe){\cdot}COMe$ (166), 144, 165, 157, and 156.

This method is very convenient, as it simply depends on three weighings, and is independent of delicate thermometric readings.

L. T. T.

Cryoscopic Behaviour of Solutions of Iodoform in Benzene and Acetic Acid. By N. v. Klobukoff (*Zeit. physikal. Chem.*, **3**, 351—353).—The author finds that the cryoscopic behaviour of solutions of iodoform in benzene and acetic acid is a perfectly normal one, the molecular reduction being, in the first instance, 49, and in the second 39.

H. C.

Inorganic Chemistry.

Chlorine from Bleaching Powder. By C. Winkler (*Ber.*, **22**, 1076—1077).—When chlorine is generated from bleaching powder and hydrochloric acid in a Kipp's apparatus, it is advisable, after using the apparatus, to blow in a little air, otherwise a slow but continuous action takes place, owing to the absorption of the chlorine by the acid.

F. S. K.

Determination of the Boiling Point of Ozone and of the Solidifying Point of Ethylene. By K. Olszewski (*Ann. Phys. Chem.* [2], **37**, 337—340).—Hautefeuille and Chappuis have shown that ozonised oxygen solidifies to a dark-blue liquid at a pressure of 125 atmospheres, and at the temperature at which ethylene evaporates under the atmospheric pressure, namely, $-102{\cdot}5°$. The ozone remains in a liquid state after the pressure has been reduced to that of the atmosphere, from which it follows that the boiling point of ozone cannot be very much lower than that of ethylene, and therefore the author hoped to be able to obtain liquid ozone by injecting ozonised oxygen into a vessel cooled to −150° at the ordinary atmospheric pressure. He found, however, that he was unable to do this. The vessel was cooled down to −151° by means of liquid ethylene, but no ozone was liquefied, being evidently prevented from doing so by the large quantity of oxygen with which it was mixed, the boiling point of oxygen being very much lower. By using liquid oxygen at the atmospheric pressure in place of ethylene, the temperature was reduced to −181·4°, and the ozone was then easily obtained, in the form of a dark-blue liquid, whilst the oxygen with which it was mixed remained uncondensed, and was allowed to escape by an opening at the top of the tube. When the ozonised oxygen was injected into a tube thus surrounded by liquid oxygen at the temperature of −181·4°, a drop of ozone could be observed in the course of a few minutes, and if the influx of gas was then stopped, and the oxygen surrounding the tube allowed to evaporate, the ozone remained liquid until the whole of the oxygen had evaporated. It was necessary in performing this experiment to cut off the supply of ozonised oxygen, as when this was not done the liquid ozone was swept out of the tube by the stream of gas. After the oxygen had completely evaporated, the temperature of the tube would be about −150°, namely, that of the liquid ethylene surrounding the tube which originally contained the liquid oxygen. At the boiling point of oxygen, the ozone remained in the form of a dark-blue liquid, which was transparent in thin layers, but became almost opaque at a thickness of about 2 mm.

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* A new substance prepared by Tiemann and Neitzel, but not yet described.

In order to determine the boiling point of the ozone, the tube containing it was removed from the apparatus, and placed in another vessel containing liquid ethylene at a temperature of −140°. The ozone was found to remain liquid until the ethylene had nearly reached its boiling point. The temperature at which the ozone began to evaporate was observed by means of a sulphurous acid thermometer, which was found to register −109°, corresponding to −106° of the hydrogen thermometer, so that the boiling point of pure ozone may be taken as −106°.

The greatest care had to be exercised in making the experiments, to prevent ozone from coming in contact with the ethylene, which would cause it to explode. In one of the experiments a drop of liquid ozone just below its boiling point exploded in this way, and the explosion was so violent that the triple glass walls of the apparatus were blown into fine dust.

When the pure ozone was allowed to evaporate, it changed into a bluish-coloured gas, which retained its colour at the ordinary temperature, and could be recondensed by immersing it in liquid ethylene.

In a former paper (Abstr., 1885, 1101) the author has described his attempts to freeze ethylene by allowing it to evaporate in a vacuum. His attempts, however, were unsuccessful, the ethylene remaining liquid and transparent at a temperature of −162° and a pressure of between 1 and 2 mm. of mercury.

He has now succeeded in solidifying ethylene by enclosing it in a tube surrounded by liquid oxygen, itself surrounded by liquid ethylene, as in the case of the experiments with ozone. The ethylene was found to solidify at about the boiling point of oxygen, −181·4°, to a white, crystalline, semi-transparent mass. When the stopcock, through which the oxygen as it evaporated was allowed to escape, was closed, so as to allow the pressure and the temperature of the oxygen to gradually increase, the solid ethylene became liquid at a pressure of 3·4 atmospheres, at which, according to the author's former researches (*Compt. rend.*, **100**, 350), the temperature of the liquid oxygen would be −169°, which may therefore be taken as the melting point of solid ethylene. G. W. T.

Action of Alkalis on the Thionic Acids. By BERTHELOT (*Compt. rend.*, **108**, 925—930).—Pentathionates in contact with excess of an alkaline hydroxide yield sodium thiosulphate, with development of heat, even at the ordinary temperature. Complete decomposition would develop +48 Cal., but the amount actually observed was +44 Cal., and hence the change is incomplete. Conversion of pentathionic acid into thiosulphuric acid by assimilation of water, $2H_2S_5O_6 + 3H_2O = 5H_2S_2O_3$, would absorb −34·6 Cal., but the increase in saturating power corresponds with an increase of +82·8 Cal. in the heat of neutralisation, and hence a balance of +48·2 Cal. in favour of the reaction.

Tetrathionates in presence of excess of alkali are slowly converted into thiosulphate and sulphite, $2Na_2S_4O_6 + 3Na_2O = 3Na_2S_2O_3 + 2Na_2SO_3$. If the reaction were complete it would be accompanied by a development of +72·6 Cal. The conversion of tetrathionic acid into thiosulphuric and sulphurous acids would absorb −18·6 Cal. As in the preceding instance the exothermic character of the reaction depends on the increase in the saturating power of the acids.

Trithionates are more stable, and at the ordinary temperature the change cannot be recognised until after the lapse of a considerable time. When heated, the trithionate is converted into thiosulphate and sulphite, $2K_2S_3O_6 + 3K_2O = K_2S_2O_3 + 4K_2SO_3$. Complete conversion corresponds with a development of +35·8 Cal. The conversion of trithionic acid into the other acids would absorb −36·2, but the increase in the heat of neutralisation is +72·0 Cal.

Sodium hydroxide has no action on the dithionates in the cold.

The thionic acids may be regarded as derivatives of condensed simple or mixed anhydrides, which are themselves derived from thiosulphuric and sulphurous acids. Thiosulphuric acid may be regarded as S_2O_2,H_2O, capable of giving rise to a series of condensed anhydrides of the general formula $nS_2O_2,n—mH_2O$, the basicity of the resulting acids being proportional to the value of m. According to this view pentathionic acid is $5S_2O_2,2H_2O$, the values of n and m being 5 and 3 respectively. When sulphurous acid, SO_2,H_2O, is likewise present, it may behave in a similar manner, and thus we should be able to obtain, amongst others, the following mixed condensed anhydrides: $4S_2O_2,SO_2,H_2O$, which is tetrathionic acid; $S_2O_2,4SO_2,2H_2O$, which is trithionic acid; $4S_2O_2,SO_2,2H_2O$, which is probably the acid obtained in the first crystallisations when preparing pentathionic acid by Debus's method; and $2S_2O_2,3SO_2,2H_2O$, which has not been isolated. This view is supported by the behaviour of the thionic acids with excess of alkaline hydroxide, and the tendency to form condensed anhydrides is illustrated by the formation of the anhydrosulphites $K_2S_2O_5$ and $Na_2S_2O_5$.

The conversion of the thionic acids into thiosulphuric acid, or into this acid and sulphurous acid, would involve an absorption of heat, and hence the change does not take place in acid solutions. In presence of excess of alkali, however, the very considerable increase in the heat of neutralisation determines the change in this direction.

C. H B.

Action of Acids on Thiosulphates. By BERTHELOT (*Compt. rend.*, **108**, 971—978).—Thiosulphates, as is well known, are decomposed by acids with liberation of sulphurous anhydride and precipitation of sulphur. The sulphur, however, exists in different allotropic modifications, the sulphurous anhydride reacts with the liberated thiosulphuric acid before it has time to decompose, and forms thionic acids, and the latter are partially dissociated by the water. It follows that the final state of the system is a condition of equilibrium between many reactions. When a solution of sodium thiosulphate is mixed with boric acid there is no sensible thermal disturbance, and the liquid remains colourless and transparent. Acetic acid likewise produces no sensible variation of temperature, but a precipitate gradually forms and increases in quantity. The quantity of iodine absorbed is always much less than would be required if all the thiosulphurous acid were decomposed into sulphurous acid and sulphur. The thiosulphate is only decomposed to a slight extent, and it follows that the heat of neutralisation of thiosulphuric acid is greater than that of acetic acid, +13·3 Cal. It is possible that an acid sodium acetate is formed, and the sulphurous anhydride which is liberated produces thionic acids by interaction with the thiosulphuric acid, and hence the great length of time required before equilibrium is established.

With sodium thiosulphate and very dilute sulphuric acid there is an immediate slight rise of temperature, followed very rapidly by the formation of a precipitate and a slight fall of temperature. The heat of neutralisation of thiosulphuric acid is therefore lower than that of sulphuric acid.

Hydrochloric acid of certain concentrations produces a slight development of heat, whilst with other concentrations there is a slight absorption of heat. The liquid becomes turbid almost immediately, owing to precipitation of sulphur. It is evident that the reaction is somewhat complicated, but it is also evident that the heat of neutralisation of thiosulphuric acid is practically the same as that of hydrochloric acid, and it may be taken as +13·8 Cal. without sensible error. The absorption of heat observed in some cases is due to the decomposition of the thiosulphuric acid, and is exactly equal to the difference between the heats of formation of thiosulphuric and sulphurous acids respectively. The quantity of iodine absorbed by the solution after various times and under various conditions is given in the form of a table. Neglecting the complications due to the action of sulphurous anhydride on thiosulphuric acid, it seems that the decomposition of the latter begins immediately, and increases with the time and with the proportion of hydrochloric acid.

The action of sulphurous acid on sodium thiosulphate in various proportions is always exothermic, although the development of heat is but slight, and it would seem that there is a division of the base between the two acids, and interaction between those portions of the acids which remain free. When the two liquids are mixed, they become yellow and sulphur is precipitated, especially if the thiosulphate is in excess. If, on the other hand, sulphurous acid is in excess, only traces of sulphur separate, and these gradually redissolve. The quantities of iodine absorbed by the liquid indicate that decomposition is not complete, but is limited by the formation of thionic acids. The latter reaction also remains incomplete in consequence of the dissociating action of the water, and it follows that when equilibrium is established, the liquid has a very complex constitution, and contains thiosulphuric acid, sulphurous acid, sulphur, and thionic acids, the base being divided between thiosulphuric and sulphurous acids. C. H. B.

Note.—Vaubel (*Ber.*, **22**, 1686—1694) gives a totally different explanation of the action of acids on thiosulphates.

C. H. B.

Preparation of Alkaline Nitrites. By G. A. Le Roy (*Compt. rend.*, **108**, 1251—1252).—The finely powdered alkaline nitrate is intimately mixed with finely powdered barium sulphide in the proportion of 4 mols. of the former to 1 of the latter, and the mixture is projected with constant stirring into an iron basin heated to dull redness. The reaction takes place with incandescence, and on extracting the cooled mass with water the nitrite dissolves and barium sulphate is left and can again be reduced to sulphide. The presence of sulphate in the sulphide moderates the reaction. C. H. B.

Phosphorous Acid. By L. Amat (*Compt. rend.*, **108**, 1056—1058).—The author has previously shown that when sodium hydrogen phosphite is heated, it yields a pyrophosphite (Abstr., 1888, 914). Other phosphites behave in a similar manner, but dehydration is more difficult and there is greater liability to decomposition.

The pyrophosphites in solution again combine with water, but by careful evaporation of a saturated solution in a dry vacuum, the salt $Na_2H_2P_2O_5$ is obtained in small crystals which act on polarised light. The conversion of sodium pyrophosphite in aqueous solution into the hydrogen phosphite takes place more rapidly the more concentrated the solution and the higher the temperature; at the ordinary temperature, complete conversion requires several days, but the change is complete in a few hours if the liquid is boiled. In dilute solutions a much longer time is required. The presence of an acid such as sulphuric acid greatly accelerates the change, and if the proportion of acid is large, the conversion is complete almost immediately. With a smaller proportion of acid, the change is more rapid the greater the concentration, the higher the temperature, and the greater the proportion of free acid present. It is complete in a few minutes if the liquid is boiled, however small the proportion of free acid. If barium pyrophosphite is decomposed by an equivalent quantity of sulphuric acid, the ratio of the pyrophosphite in the liquid is 1 : 0·74; after two hours, 1 : 2·4; and after 16 hours all the pyrophosphite has disappeared. The change is immediate if the liquid is boiled.

C. H. B.

The Presence of Sodium Sulphate in the Atmosphere. By F. PARMENTIER (*Compt. rend.*, **108**, 1113—1116).—The fact that supersaturated solutions of sodium sulphate crystallise if exposed to the air, whilst supersaturated solutions of many other salts remain liquid for some time under the same conditions, is generally taken as proof of the presence of minute crystals of sodium sulphate in the atmosphere.

The author has observed the formation of very light crystals of sodium sulphate more than 20 cm. long, on the walls of rooms, &c., at the hot springs of Royat, especially where the walls were covered with plaster, the superficial layer of which has been converted into calcium carbonate. The water contains sodium hydrogen carbonate and sodium chloride, and it is most probable that the sodium sulphate is formed by double decomposition with calcium sulphate, and then effloresces in a manner similar to potassium nitrate but in its own crystalline form. Similar efflorescence can be obtained by moistening a porous plate with a saturated solution of sodium sulphate. After several crystallisations the plate disintegrates, and a similar phenomenon is observed at Royat even with the hardest stones.

The facts that the effloresced crystals are extremely light and that the formation of a similar efflorescence probably takes place in many places, seem to the author to account for the existence of the crystals of sodium sulphate in the atmosphere. C. H. B.

Note.—It is well known that sulphates exist in the air over and near the sea, owing to the evaporation of the fine spray (see Angus Smith's *Air and Rain*). C. H. B.

Action of Alkaline Arsenates on the Alkaline Earths. By LEFÈVRE (*Compt. rend.*, **108**, 1058—1060).—Barium oxide dissolves readily in fused potassium metarsenate, and the product consists of crystals which alter rapidly in contact with water, yielding small opaque crystals of the composition $BaHAsO_4 + H_2O$. If the unaltered alkaline arsenate is removed by treatment with glycerol, the residue consists of rhombic prisms of the compound $Ba_2As_2O_7$, which is analogous to the phosphate formed under the same conditions. The product is the same when potassium chloride is added to the mixture, provided that the proportion of metarsenate is not lower than 60 per cent, otherwise the chloride attacks the product and forms a chloroarsenate. Barium chloride gives the same product as the oxide.

Potassium orthoarsenate or pyroarsenate mixed with sufficient potassium chloride to make the mass fusible, yields small, transparent prisms of the compound $KBaAsO_4$, analogous to the phosphate formed under similar conditions. The proportion of orthoarsenate must not be lower than 8 per cent., nor that of the pyroarsenate lower than 18 per cent., or the products will contain chlorine.

Sodium metarsenate behaves in the same way as the potassium salt. Sodium orthoarsenate or pyroarsenate yields the normal arsenate $Ba_3(AsO_4)_2$ in large lamellæ.

Strontium oxide with potassium metarsenate yields the compound $Sr_2As_2O_7$, and with the orthoarsenate or the pyroarsenate the compound $KSrAsO_4$. Sodium pyroarsenate behaves in the same way, and yields the compound $NaSrAsO_4$ in dendritic crystals. Sodium metarsenate yields a mixture of the compounds $Sr_2As_2O_7$ and $Sr_3(AsO_4)_2$. The latter is easily obtained in long, transparent, rhombic prisms by using sodium orthoarsenate.

Calcium oxide yields similar products. Potassium metarsenate forms the compound $Ca_2As_2O_7$, which is much less readily attacked by water than the barium and strontium salts; the pyro- and orthoarsenate yield the salt $KCaAsO_4$. Sodium metarsenate yields the compound $3CaO,3Na_2O,2As_2O_5$; the pyroarsenate and orthoarsenate produce the double arsenate $CaNaAsO_4$.

In all cases in which a chloride is present, the proportion of arsenate must exceed a certain minimum or the product will contain chlorine. This minimum is highest in the case of calcium and lowest in the case of barium, strontium being intermediate. C. H. B.

Potassium Magnesium Bromide. By W. FEIT (*J. pr. Chem.* [2], **39**, 373—376).—Löwig described a salt, $2KBr,MgBr_2 + 6H_2O$, but this does not correspond with carnallite, $KCl,MgCl_2 + 6H_2O$. The author has succeeded in preparing the salt $KBr,MgBr_2 + 6H_2O$ by shaking a saturated solution of magnesium bromide with finely powdered potassium bromide for four days, and also by mixing saturated solutions of 12 parts of magnesium bromide in cold water and 1 part of potassium bromide in hot water.

In the first case magnesium sulphate was shaken with the magnesium bromide solution before the potassium bromide was added. The magnesium sulphate thus dissolved served as an indicator to show how much mother-liquor was left with the crystals, which could only be drained as they are decomposed by washing. Thus, after the crystals had been drained they contained 0·22 per cent. of sulphuric anhydride, whilst the mother-liquor contained 0·91 per cent.; the crystals, therefore, still contained 24·1 per cent. of mother-liquor, which was allowed for in the analysis.

The author never obtained Löwig's salt. A. G. B.

Formation of Mercurammonium Chlorides. By G. ANDRÉ (*Compt. rend.*, **108**, 1108—1110 and 1164—1167).—The action of ammonia on mercuric chloride has already been investigated (this vol., p. 570). If potassium hydroxide is present, so that some mercuric oxide is formed, the product contains dimercurammonium chloride, NHg_2Cl. The solutions employed contained, as a rule, one-eighth of a gram-molecule per litre. When mercuric chloride is mixed with an equal volume of potash solution and then with the same volume of ammonium chloride solution, and the precipitate, which becomes quite white, is washed and dried at 100°, it has the composition $NHg_2Cl,2NH_2HgCl,NH_2Hg\cdot O\cdot HgCl$. If the mercuric chloride and ammonium chloride are first mixed and the potash added afterwards, the precipitate remains yellowish, and whether filtered off after a few minutes or after several hours, has the composition $NHg_2Cl,NH_2HgCl,NH_2Hg\cdot O\cdot HgCl$. The smaller the excess of ammonium chloride the greater the proportion of NHg_2Cl. If equal volumes of the mercuric chloride and potash solution are mixed and heated to boiling for some minutes, then mixed with an equal volume of ammonium chloride and again boiled for a short time, the precipitate has the composition $NHg_2Cl,NH_2Hg\cdot O\cdot HgCl$, a result due to the conversion of mercurammonium chloride, NH_2HgCl, into the compound $NH_2Hg\cdot O\cdot HgCl$ when heated with water.

Employing solutions of the same strength as in previous cases, 200 c.c. of mercuric chloride solution was mixed with 150 c.c. of potassium hydroxide solution and then with 100 c.c. of ammonia solution, agitated for an hour and a half, filtered, washed, and dried at 100°. The precipitate has the composition

$$NHg_2Cl + NH_2Hg\cdot O\cdot HgCl,$$

is not affected by boiling water, and does not alter even if heated in a current of air at 140° for two hours.

300 c.c. of potash solution was mixed with 600 c.c. of ammonia and 600 c.c. of mercuric chloride was added. The precipitate was at first yellow but soon became white. Analysis of the filtrate and the precipitate showed that the latter had the composition $NHg_2Cl + 2NH_2HgCl + NH_2Hg\cdot O\cdot HgCl$. If only ammonia is in excess, so that no ammonium chloride is found in the filtrate, the proportion of mercury in the precipitate becomes less, the mercurammonium chloride, NH_2HgCl, being completely decomposed. The same result is obtained whether the mercuric chloride is added to the mixture of potash and ammonia or potash is added to a mixture of the other two.

200 c.c. of mercuric chloride was mixed with 400 c.c. of ammonia and the precipitate washed by decantation and mixed with one molecular proportion of potassium hydroxide. After agitation for one and a half hours, the precipitate was washed and dried at 110°. Analysis of the filtrate and the precipitate shows that mercurammonium chloride is decomposed by potassium hydroxide, whilst at the same time it is decomposed by water with formation of Millon's salt and ammonium chloride, the composition of the precipitate being $NHg_2Cl + 2NH_2\cdot Hg\cdot O\cdot HgCl$.

In all these reactions, when ammonium chloride is formed mercurammonium chloride is also produced, but if ammonium chloride is not formed the precipitates contain only the compounds NHg_2Cl and $NH_2Hg\cdot O\cdot HgCl$. The dimercurammonium chloride is converted by excess of ammonium chloride into mercurammonium chloride.

C. H. B.

Solubility of Glass in Water. By F. MYLIUS and F. FOERSTER (*Ber.*, **22**, 1092—1112).—The authors have very carefully examined the solubility in hot and cold water of a large variety of glasses of very varying composition. The glass experimented on was roughly powdered and then sifted by means of two sieves of 72 and 121 meshes respectively to the square centimetre. The portions passing through the coarser sieve but retained by the finer, were tolerably equal in size of grain, and it was safe to assume that in equal volumes of the different glasses thus prepared the total surface was approximately equal. The minimum surface for the quantities taken (18 to 20 grams) was 763 square centimetres.

The results show that glass *as such* is not soluble, the solution always being accompanied by decomposition, and the ratio of the various constituents in solution is quite different to that in the original glass. The action is essentially a chemical one. For instance, in an experiment where 2·5 grams of so-called soda water-glass was treated with water and the solution separated into fractions, the result was: Original glass, $Na_2O : SiO_2 = 34·07 : 65·93$: Fraction I, 88·13 : 11·87; fraction II, 41·64 : 58·33; fraction III, 30·31 : 69·69; fraction IV, 3·1 : 96·7. Fraction I was obtained by the treatment of the powdered glass with cold water for five minutes; II, by washing with hot water; III, by 15 minutes' boiling; IV was the insoluble residue left.

The principal conclusions deducible from the experiments are:—

(i.) Water-glass is decomposed by water into free alkali and silicic acid, a certain proportion (varying with the time of action, concentration, and temperature) of the latter becoming hydrated and dissolved.

(ii.) Potash-glasses are far less soluble than soda-glasses, but the difference decreases with increase of the proportion of lime present.

(iii.) Soda and potash are united in glass both to the silica and the lime. The resistance of glass towards the action of water is dependent on the presence of double silicates of soda or potash and lime.

(iv.) Of all sorts of glass, the plumbiferous flint-glasses are least soluble in boiling water.

(v.) The relative resistance of glasses is different towards hot and cold water.

Tables are given in the original showing the solubility, as determined by digestion with boiling water for five hours, of various glasses commonly found in commerce, and the chemical composition of the same glasses.

L. T. T.

Formation of Manganese Oxides in the Wet Way. By A. Gorgeu (*Compt. rend.*, 108, 948—951).—When manganous hydroxide is exposed to air in presence of an excess of a manganous salt, it yields the manganese manganite $2MnO,MnO_2$, with a variable quantity of water. In presence of oxygen instead of air, oxidation is more rapid and the proportion of oxygen in the product is slightly higher. The product slowly absorbs oxygen from the air or from oxygen at the ordinary temperature, but even after 12 years the proportion of oxygen does not exceed that required by the formula MnO_2,MnO. In presence of alkalis or alkaline earths, as is well known, manganous hydroxide will take up a much larger proportion of oxygen.

Solutions of manganous salts gradually become turbid when exposed to air, especially in diffused light, and still more rapidly in bright sunlight. The change does not take place in an atmosphere of hydrogen. With the chloride, sulphate, and acetate, the precipitate has the composition MnO,MnO_2, but with the nitrate, its composition is $2MnO,3MnO_2$. The quantity of manganese precipitated in this form is only a small fraction of that present in the liquid. In concentrated solutions the amount precipitated is still less, and hence it would seem that precipitation is due to the action of oxygen on a manganese salt partially dissociated by water.

Solutions of manganous sulphate, nitrate, chloride, bromide, and iodide may be boiled without undergoing any noteworthy alteration, but the acetate yields more precipitate than at the ordinary temperature. The precipitate has the composition MnO,MnO_2, the acetic acid is continuously given off during boiling, hence it would seem that manganous oxide is liberated in consequence of the dissociation of the salt, and behaves like the manganous hydrate thrown down by alkalis.

Iodine dissolved in a solution of potassium iodide has little action on manganous hydroxide, scarcely attacks manganous carbonate, and has no action on the acetate and salts of the strong acids. Chlorine acts rapidly on the hydroxides and on all the salts. The most concordant results were obtained with chlorine-water and manganous carbonate. With the carbonate in excess, the product was MnO,MnO_2, but with chlorine in excess the more highly oxidised products, $MnO,4MnO_2$ and $MnO,5MnO_2$, were obtained. Up to the latter point the mixture remained neutral, and the manganous chloride formed was equivalent to the oxygen which entered into combination. The further action of chlorine is indirect, hydrochloric acid and not manganous chloride being formed.

Bromine behaves in a similar manner, but the reaction is slower.

C. H. B.

Action of Air on Manganous Carbonate. By A. GORGEU (*Compt. rend.*, **108**, 1006—1009).—Native manganous carbonate or *diallogite* is very stable, and remains unaltered after contact with aerated water for three years. Precipitated manganous carbonate which has become crystalline, remains in contact with aerated water at the ordinary temperature without forming any peroxide. Even at 100° the amount of peroxide formed is very minute. If the precipitated carbonate remains in contact with aerated water for 10 years, about one-third is decomposed, and the product has the composition MnO,MnO_2. Two specimens containing respectively 80 and 70 per cent. of manganous carbonate were exposed to air in the dry state for eight years; in the first case 33 per cent. and in the second 14 per cent. of manganous carbonate remained, the rest having been converted into the oxide MnO,MnO_2.

The oxide MnO,MnO_2 can be obtained by the direct combination of manganous hydroxide and hydrated peroxide, and undergoes no change if exposed to air for five months in the dry state or under water.

Manganous carbonate when exposed to air at the ordinary temperature, yields no oxide higher than MnO,MnO_2, and a similar result has previously been obtained with the hydroxide (preceding Abstract).

When manganous carbonate is exposed to air at 100° for 250 hours only two-thirds remains unaltered, the rest being converted into an oxide which contains considerably more oxygen than is required by the formula MnO,MnO_2. At 200°, after 30 hours, the oxide formed contains 92 per cent. of manganese peroxide. The oxide MnO,MnO_2 undergoes no further oxidation at 100°. C. H. B.

Some Metallic Sulphides. By A. GAUTIER and L. HALLOPEAU (*Compt. rend.*, **108**, 1111—1113; compare this vol., p. 677).—The action of carbon bisulphide vapour on metallic nickel at a bright-red heat yields two substances, which are easily separated. One is black, friable, granular nickel sulphide, the other is nickel subsulphide, Ni_2S, in the form of a dense, resisting, yellowish, metallic substance, which has undergone fusion but can be finely powdered. It is not magnetic, and it has a hardness somewhat greater than 4. The powdered substance consists of small, tuncated prisms with a square base; sp. gr. at 0° = 5·66. The powder is dull-green, and has lost the metallic lustre of the mass. It is not decomposed by hot or cold water, and is very slowly attacked by dilute or concentrated hydrochloric acid, even when heated. Prolonged contact with vapour of carbon bisulphide at a red heat converts it into nickel sulphide, NiS.

Arfvedson described nickel subsulphide as magnetic, but his product probably contained unaltered nickel, and it has generally been regarded as a mixture of nickel and nickel sulphide.

The black substance from which the nickel subsulphide is separated consists of 36 per cent. of a nickel carbide insoluble in aqua regia and containing 20·05 per cent. of nickel, and 64 per cent. of nickel sulphide, NiS.

The action of carbon bisulphide vapour on crystallised chromium at a bright-red heat yields chromic sulphide, Cr_2S_3, a dark-grey, hard, sonorous substance, which resembles graphite in appearance, and makes a mark on paper. It is mixed with unaltered chromium, which is removed by treatment with aqua regia.

The action of carbon bisulphide vapour on lead at a little above a red heat yields brilliant crystals of galena. The cool part of the tube contains yellow crystals, which yield carbon bisulphide and lead sulphide when treated with an acid, and hence would seem to be a lead thiocarbonate. C. H. B.

Crystallised Orthosilicates of Nickel and Cobalt. By L. BOURGEOIS (*Compt. rend.*, **108**, 1177—1178).—The author's method consists in heating an intimate mixture of a metallic oxide with the corresponding chloride and a large excess of amorphous silica to bright redness in a Perrot's furnace for several hours. None of the metallic oxide remains unattacked, and the excess of silica is removed by treatment with a solution of an alkaline hydroxide.

Cobalt oxide and chloride yield the orthosilicate Co_2SiO_4, in the form of a beautiful, violet powder, of sp. gr. 4·63. It consists of minute, deep-violet, non-dichroic crystals, with forms and optical properties recalling those of peridote. It readily gelatinises with acids.

Nickel orthosilicate, Ni_2SiO_4, obtained in the same way, forms minute, greenish-yellow crystals, strongly resembling those of peridote, but darker in colour; sp. gr. 4·85.

It is noteworthy that neither nickel nor cobalt yields an acid silicate, even in presence of a large excess of silica, and in this respect they resemble iron, but Fouqué has obtained a double silicate of cobalt and calcium which seems to be an acid salt.

Cadmium yields a crystalline silicate under similar conditions, but no crystalline product could be obtained with cerium, lanthanum, didymium, or uranium. C. H. B.

Preparation of Chromic Chloride. By A. VOSMAER (*Zeit. anal. Chem.*, **28**, 324).—Chlorine is passed over heated ferrochrome in a glass tube. Ferric chloride being more, and manganous chloride less, volatile than chromic chloride, the latter is obtained in a state of great purity. M. J. S.

Metatungstic Acid. By E. PÉCHARD (*Compt. rend.*, **108**, 1167—1170).—Metatungstic acid has a very energetic acid function; its heats of neutralisation by one equivalent of an alkali or alkaline earth, with formation of metatungstates of the general formula $M_2O,4WO_3$, are given in the following table, with the corresponding values for nitric and sulphuric acids:—

	Potassium oxide.	Sodium oxide.	Strontium oxide.	Barium oxide.
Sulphate.....	15·7	15 85	15·4	18·4 (pptd.)
Metatungstate	14·05	14·24	14·76	15·4
Nitrate......	13·8	13·7	13·9	13·9

The addition of a further quantity of base gradually converts metatungstates into orthotungstates, the change being complete with four equivalents of base.

In the case of sodium, $Na_2O,4WO_3$ diss. + 6NaOH diss. = $3Na_2WO_4$ diss., develops +6·72 Cal. The addition of a further quantity of alkali causes no appreciable thermal disturbance.

When one equivalent of metatungstic acid is mixed in the calorimeter with four equivalents of barium hydroxide, the thermometer rises rapidly and attains a maximum, whilst a white, gelatinous precipitate separates and slowly becomes crystalline, the temperature gradually falling during the second phase. The gelatinous precipitate has the composition $BaWO_4 + 2H_2O$, whilst the crystalline precipitate is $BaWO_4 + H_2O$. The same precipitate can be obtained by the action of barium hydroxide on barium metatungstate. It is obvious that the action of barium hydroxide on metatungstic acid takes place in three phases, namely: (1) formation of the metatungstate, (2) conversion of the metatungstate into the gelatinous orthotungstate, (3) crystallisation of the orthotungstate; the total development of heat being +39·0 Cal. It follows that $BaO,4WO_3$ diss. +

$3Ba(OH)_2$ diss. = $4BaWO_3$ pptd., develops + 8·2 Cal. Barium orthotungstate is neutral to phenolphthaleïn, and hence the latter can be used as an indicator for the titration of tungstic acid by barium hydroxide. The metatungstate is acid to this indicator.

C. H. B.

Variations in the Acid Function of Stannic Oxide. By L. VIGNON (*Compt. rend.*, **108**, 1049—1052).—Stannic acid prepared from stannic chloride, metastannic acid prepared by the action of nitric acid on tin, and ignited stannic oxide were treated in a calorimeter with excess of potassium hydroxide.

Stannic Acid.—In some cases the stannic acid was formed from stannic chloride in the calorimeter by means of the reaction $SnCl_4$ + $4KHO$ + Aq = H_2SnO_3 + $4KCl$ + H_2O + Aq, the heat developed being + 51·3 Cal. Five quantities of 10 c.c. each of a solution containing 45·2 per cent. of $SnCl_4,5H_2O$, were treated in different ways, namely, (1) kept for 24 hours, (2) kept for 17 days at the ordinary temperature, (3) kept at the ordinary temperature for 30 days, (4) heated in sealed tubes at 150° for four hours with four times its volume of water, and (5) heated at 150° in sealed tubes for four hours with 4 mols. potassium hydroxide and four times its volume of water. The heat of neutralisation by excess of potassium hydroxide (H_2SnO_3 + 4KOH) was then determined, with the following result:—

(1.)	(2.)	(3.)	(4.)	(5.)
32·7	31·3	29·6	25·7	21·3

If 10 c.c. of the freshly prepared stannic chloride solution is mixed with 26 c.c. of binormal potassium hydroxide, the liquid remains quite clear, yields no trace of free hydrochloric acid on distillation, but decomposes carbonates in the cold. The addition of a cold, concentrated solution of sodium sulphate completely precipitates the stannic acid. The different heats of neutralisation are due to polymerisation of the acid. If it is left in contact with water free from potassium chloride and hydrochloric acid, it undergoes further change. Two samples precipitated by sodium sulphate were kept in water, one for 24 hours at 15° and the other for an hour at 95°; the heats of neutralisation were +8 Cal. and +4 Cal. respectively.

Metastannic Acid.—This acid was employed in three forms, namely: (1) after drying at the ordinary temperature, when it has the composition $Sn_5O_{11}H_2,20H_2O$; (2) after drying at 110°, when it has the composition $Sn_5O_{11}H_2,4H_2O$; (3) after heating in sealed tubes at 250° with four times its weight of water for four hours. The heats of neutralisation by potassium hydroxide were

(1.)	(2.)	(3.)
11·5 Cal.	10·8 Cal.	5·3 Cal.

Stannic oxide, prepared by heating metastannic acid to bright redness for an hour, gave a heat of neutralisation of +1·0 Cal.

It would seem that a whole series of stannic acids exists, the extremes being the acid completely soluble in water and ignited stannic oxide. The composition of metastannic acid indicates that condensation does not take place by elimination of water, but is the result of molecular rearrangement which produces a gradual diminution of the activity of the acid function. The polymerisation may be regarded as due to the energetic acid function of the simple acid, which unites with a number of its own molecules which play the part of a base. Probably silica and alumina and other metallic oxides behave in the same way. C. H. B.

Combination of Nitrogen Oxides with Metallic Chloride. By A. Besson (*Compt. rend.*, **108**, 1012).—Nitric oxide combines directly, and with great development of heat, with antimony pentachloride, forming a yellow, crystalline compound, $2SbCl_5,NO$, which is decomposed by water with evolution of nitric oxide and some nitrogen peroxide. When heated, it partially volatilises, and leaves a residue of antimony tetroxide. The compound is obtained in crystals by heating in a sealed tube at 100° for several hours.

Nitric oxide also combines with bismuth chloride, aluminium chloride, and ferric chloride, forming yellow compounds which are obtained in crystals by heating them in sealed tubes and are decomposed by water.

Nitrogen peroxide combines directly with antimony pentachloride with great development of heat, forming a compound, $3SbCl_5,2NO_2$, which is obtained in pale yellow crystals by heating it in a sealed tube at 100°.

Nitrogen peroxide also combines with antimony trichloride, bismuth chloride, ferric chloride, and aluminium chloride, forming compounds which are decomposed by water. They are less stable than the corresponding compounds of nitric oxide, and are converted into oxides at a comparatively low temperature. C. H. B.

Platinum Tetrachloride. By L. Pigeon (*Compt. rend.*, **108**, 1009—1011).—Finely divided spongy platinum mixed with somewhat less than its own weight of selenium is placed in a stout glass tube one-third filled with arsenic trichloride, and a current of chlorine is passed in, the tube being gradually heated until the liquid boils. The platinum is rapidly and completely dissolved, and the tube is then sealed and heated at 250° for several hours. After cooling, the tube contains a pale yellow liquid, orange-yellow crystals, and also, if the selenium is in excess, colourless crystals. The crystals are separated and heated in a vacuum at 110°. They then consist of platinum tetrachloride and selenium tetrachloride, and are heated at 360° in a current of chlorine, when selenium chloride sublimes and anhydrous platinum tetrachloride remains as a brown, very hygroscopic powder. At 440° it is converted into the dichloride. If platinum selenide is used instead of a mixture of platinum and selenium, no action takes place even at 300°; if selenium is omitted altogether the platinum is not completely attacked, but the action becomes complete if selenium is added. The action of chlorine on finely divided platinum at 360° is incomplete, the tetrachloride and dichloride are formed, but a considerable portion of the metal remains unattacked. C. H. B.

Atomic Weight of Ruthenium. By A. JOLY (*Compt. rend.*, **108**, 946—948).—Ruthenium was converted into the peroxide and thus separated from platinum, iridium, rhodium, and palladium. The peroxide was converted into the sesquichloride by treatment with concentrated hydrochloric acid at 100°, and this was converted into potassium nitrosochloride (this vol., pp. 352 and 678). In this latter process all the osmium is volatilised as peroxide. The ruthenium nitrosochloride was treated with chlorine in the presence of potassium hydroxide, and was thus converted into the peroxide, which was purified by distillation and then treated with hot water. The oxide thus obtained, Ru_4O_9, was dried and heated in oxygen at 500°, in order to convert it into the dioxide. The atomic weight was determined (1) by reducing the dioxide in hydrogen (five determinations), (2) by reduction of the nitrososesquichloride in hydrogen (two determinations), and (3) by reduction of the ammonium nitrosorutheniochloride (two determinations). The values obtained were 101·41, 101·49, and 101·39 respectively, when $O = 15·96$. The atomic weight of ruthenium may, therefore, be taken as 101·4 if $O = 15·96$, or 101·65 if $O = 16$. This lower result is doubtless due to the complete separation of the osmium during the formation of the nitrosochloride. C. H. B.

Mineralogical Chemistry.

Platiniferous Nickel Ore from Canada. By F. W. CLARKE and C. CATLETT (*Amer. J. Sci.*, **37**, 372—374).—The authors have examined a number of samples of nickel ores from the Sudbury mines, Ontario. The predominating constituent was a nickel mineral that gave on analysis the following results:—

Ni.	Fe.	SiO_2.	Cu.	S.	Total.	Sp. gr.
41·96	15·57	1·02	0·62	40·80	99·97	4·541

These figures are in accord with the formula Ni_3FeS_5, or, in other words, the mineral has the composition Ni_4S_5, with about one-fourth of the nickel replaced by iron. The only species with which this agrees is Laspeyres's polydimite. The mass, from which the mineral was selected for the above analysis, averaged 35·39 per cent. of nickel and 5·20 per cent. of copper. It was assayed for platinum, the result being that 2·55 oz. to the ton or 0·0087 per cent. of platinum was found. That platinum should exist in appreciable quantities in an ore of such character is remarkable; but whether it could be profitably extracted is an open question. B. H. B.

Genesis of Alluvial Gold. By E. COHEN (*Jahrb. f. Min.*, 1889, i, Ref., 439—440, from *Mit. Ver. f. Neuvorpommern u. Rügen*, **19**, 198). —Whilst all geologists agree that the gold found in alluvial deposits is derived from older rocks, opinions differ as to the manner in which the gold has been liberated and concentrated—whether mechanical or chemical processes have prevailed. After a careful study of the literature of the subject, aided by his own experience, the author comes to the conclusion that by far the greater portion of alluvial gold has been liberated by the mechanical destruction of older deposits, and has been mechanically deposited. On the other hand, separation from solutions undoubtedly occurs, although only in a subordinate manner.

The author concludes his paper with the following results of some analyses of gold from the North Transvaal:—

	Residue.	Ag.	Au.	Cu.	Fe.	Total.
I..	0·02	5·16	94·48	0·25	trace	99·91
II..	0·78	6·49	91·38	0·09	trace	98·74
III*a*..	0·07	4·64	95·16	—	trace	99·87
III*b*..	0·07	4·57	94·87	0·11	trace	99·62

I. Vein gold from Button's reef, near Marabastad. II. Alluvial gold from Button's Creek, derived from the reef. III. Alluvial gold in small flakes and grains. The percentage of silver in the vein gold is midway between that in the two samples of alluvial gold.

B. H. B.

Modifications of Zinc Blende. By F. v. SANDBERGER (*Jahrb. f. Min.*, 1889, i, Mem., 255—258).—The author finds that zinc sulphide always occurs in mineral veins in several generations. The oldest, as a rule, consists of brownish-black regular blende with a dark brown streak, and is associated with quartz and spathic iron ore, as at Holzappel, Ems, Oberlahnstein, &c. Sometimes the three minerals are regularly banded together. At Přibram, under this, there is an older hexagonal blende, known as spiauterite or wurtzite, which always contains lithium sulphide. In the regular blendes from various localities, the author has detected iron, manganese, cadmium, tin, and copper. Thus blende from the Friedrichssegen mine at Oberlahnstein (sp. gr. 3·98) gave on analysis:—

S.	Zn.	Fe.	Mn.	Pb.	Cu.	Cd.	Sn.	Total.
33·012	59·560	5·252	0·620	0·630	0·482	0·047	0·052	99·655

The second generation of regular blende chiefly occurs in fissures in the first in the form of adamantine crystals of a light colour, usually red or yellow. Transparent red crystals from the Rosenberg mine at Braubach gave on analysis:—

S.	Zn.	Fe.	Cu.	Cd.	Total.	Sp. gr.
32·50	66·61	0·54	0·04	trace	99·69	4·08

A second younger generation of zinc sulphide is the so-called *Schalenblende*. This has been found to be a mixture of regular and hexagonal zinc sulphide in varying quantities. An analysis of this mineral (sp. gr. 4·05) from Brilon, in Westphalia, gave—

S.	SO_3.	Zn.	Cd.	Cu.	Fe.	Li + Na.	O.	Total.
30·04	0·10	65·09	trace	0·32	0·56	0·70	(3·19)	100·00

The substance thus consists of 77·8 per cent. of zinc sulphide, 14·94 per cent. of zinc oxide, and a small quantity of alkalis. B. H. B.

Strontianite from Altahlen. By C. VRBA (*Zeit. Kryst. Min.*, **15**, 449—454).—The author recently purchased a specimen described as aragonite from the Wilhelmine mine, Altahlen, in Westphalia. Although the crystals exactly resembled those of the aragonite twins of Herrengrund in Hungary, the mineral was found on analysis to be strontianite, the analytical results being as follows:—

$SrCO_3$.	$CaCO_3$.	$FeCO_3$.	Total.	Sp. gr.
93·30	6·37	0·87	100·54	3·691

These results are in good accord with the formula $10SrCO_3,CaCO_3$. The crystals are the largest of strontianite yet met with, being 20 mm. high and 16 mm. broad. In colour they are pale yellowish-white, and translucent. The predominating planes are ∞P, $\infty\breve{P}\infty$, and $0P$. Other subordinate planes, mostly only appearing as narrow facettes, are $\frac{1}{3}P$, P, $\frac{1}{2}\bar{P}\infty$, $\frac{1}{2}\breve{P}\infty$, $\frac{2}{3}\breve{P}\infty$, $\breve{P}\infty$, $2\breve{P}\infty$, and $3\breve{P}\infty$. The last is new for strontianite. B. H. B.

Minerals from the Central Ural. By A. SAYTZEFF (*Zeit. Kryst. Min.*, **15**, 560, from *Mem. com. géol. St. Pétersbourg*, 4, No. 1).—In a geological description of the districts of Rewdinsk and Werch-Issetsk, the author gives several analyses of minerals. Amongst these are the following:—

	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	Insoluble.	Total.
I..	5·00	76·81	13·00	2·63	97·44
II..	49·80	48·11	1·27	0·06	99·24
III..	50·41	47·49	0·72	—	98·62

I. Breunerite from the talc-schist at the mouth of the Bynarka; II. Dolomite from the same rock at Werchne-Tagilsk; and III, from the serpentine of the chrome-iron ore mine at Werch-Neiwinsk. B. H. B.

Apatite from Pisek. By C. VRBA (*Zeit. Kryst. Min.*, **15**, 463—469).—Apatite is one of the commonest minerals met with in the cavities in the pegmatite of Pisek. The crystals are rich in planes, the list given by the author including $\frac{4}{5}P$ a form new for this species. Analysis of transparent, pale bluish-green crystals (sp. gr. 3·094) gave the following results:—

P_2O_5.	CaO.	MgO.	F.	Cl.	Insoluble.	Total.
41·35	55·15	trace	3·56	trace	0·81	100·87

from which the author deduces the formula $3Ca_3P_2O_8,CaF_2$. Since chlorine is found only in traces, the Pisek apatite appears to be a pure fluorine apatite. B. H. B.

Enrichment of Phosphatic Chalk: Origin of the Rich Phosphate of Beauval. By A. NANTIER (*Compt. rend.*, **108**, 1174—1175).—When a phosphatic chalk is simply levigated with water, a residue is obtained containing a large percentage of calcium phosphate. Calcium phosphate extracted in this way from the phosphatic chalk at Beauval has a composition similar to that of the phosphatic pockets in the same locality, and hence it seems highly probable that the latter are residues resulting from the percolation of water charged with carbonic anhydride through the phosphatic chalk.

C. H. B.

Minerals from the Douglashall Salt Mine. By C. OCHSENIUS (*Jahrb. f. Min.*, 1889, i, Mem., 272—275).—The author describes and gives analyses of a number of minerals found in the Douglashall mine near Stassfurt. Bloedite (astracanite) occurring below the rock-salt on kainite gave on analysis—

Na_2SO_4.	$MgSO_4$.	K_2SO_4.	NaCl.	H_2O.	Insoluble.	Total.
34·3	30·5	5·3	12·0	17·7	0·2	100·0

A crystallised potassium sodium sulphate (glaserite?) gave the following results:—

K_2SO_4.	Na_2SO_4.	$MgSO_4$.	NaCl.	Insoluble.	Water.	Total.
58·7	19·5	3·4	14·4	0·1	3·9	100·0

Amongst the other minerals described by the author are:—Crystallised iron boracite, red rock crystal, bischofite, tachyhydrite, krugite, and polyhalite.

B. H. B.

Barium Sulphate. By A. LACROIX (*Comp. rend.*, **108**, 1126—1128).—Barytes crystallises in the rhombic system, but near Templeton, Quebec, Canada, the author found barium sulphate in monoclinic crystals. It has three cleavages: one with a nacreous lustre, very easy, and giving thin lamellæ on mere pressure with the fingers; a second, less easy, and with a vitreous lustre; and a third, more difficult, but somewhat distinct in thin sections. The optical properties show that the crystals are monoclinic; the angles are (001) (010) = 90°, (100) (010) = 90°, (001) (100) = 102—103°. They show polysynthetic macles with the face (100) as the face of association, and an angle of rotation of 180° round the axis normal to this face. The face (010) shows numerous hemitropic lamellæ similar to those observed with triclinic felspars. The plane of the optical axes is normal to the face (010), the angle between the axes being nearly 90°. The indices of refraction for the sodium and thallium lines are as follows:—

	Na.	Tl.
n_g	1·6459	1·6351
n_m	1·6413	1·6305
n_p	1·6364	1·6252

The nacreous lustre of the cleavage along (100) is very remarkable. The crystals are transparent in sections 5 mm. thick; the hardness and chemical properties agree with those of barytes. Analysis showed that the mineral contained neither chlorine nor fluorine, and had the composition $BaSO_4$ 96·9, $SrSO_4$ 2·0, $CaSO_4$ 1·2 = 100·1, sp. gr. at 15° = 4·39. This is the first example of dimorphism in the sulphates of the alkaline earths, and the author proposes to call this variety Michel-levite in honour of Michel Levy. C. H. B.

So-called Jadeite from Switzerland. By A. B. MEYER (*Jahrb. f. Min.*, 1889, i, Mem., 270—271).—The author shows that the supposed nephrite or jadeite from the Piz Longhin, Bergell, is a dense idocrase, analysis of which gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
38·36	21·65	2·08	33·76	2·43	1·25	99·53	3·34

B. H. B.

Meteoric Iron from Portugal. By E. COHEN (*Jahrb. f. Min.*, 1889, i, Mem., 215—223).—The author has analysed portions of the various constituents of the meteoric iron from S. Julião de Moreira, Minho, Portugal. The nickel iron, after subtraction of the schreibersite, gave—

Fe.	Ni.	Co.	Cu.	Total.
92·92	5·98	1·01	0·09	100·00

Similar composition is exhibited by several other hexahedral irons. The crust of the meteorite was found to consist of a mixture of nickel iron and schreibersite with products of their decomposition. The iron sulphide could not be purified; it was found to consist of 60·14 per cent. of troilite and 37·58 per cent. of ferric oxide. The schreibersite gave on analysis—

P.	Fe.	Ni + Co.	Total.
15·74	69·54	14·86	100·14

The high percentage of cobalt (1·31) is remarkable. The analytical results are in good accord with the formula $Fe_5(NiCo)P_2$.

B. H. B.

Organic Chemistry.

Hydrocarbons of the C_nH_{2n-2} Series. By A. BÉHAL (*Ann. Chim. Phys.*, **16**, 200—211 and 347—378).—*Hydrocarbons of the Diethylene Series.*—Hexylene oxide, identical with the compound prepared by Würtz (*Ann. Chim. Phys.* [4], **2**, 129), condensation products of diallyl in small quantities, and diallylsulphuric acid are formed when diallyl (b. p. 58—60°) is added drop by drop to well-cooled sulphuric acid, the whole being frequently agitated. (Compare Jekyll, *Bull. Soc. Chim.*, **15**, 233.) The solution is diluted with ice, neutralised with calcium carbonate (or better with potash), filtered and distilled. Hexylene oxide collects in the receiver, and the aqueous solution remaining contains *calcium diallyl sulphate*, $(C_6H_{11}SO_4)_2Ca$, which is precipitated on adding alcohol to the concentrated solution. The *barium* salt, $(C_6H_{11}SO_4)_2Ba$, turns brownish at 100°. The *potassium* salt was also prepared. These three salts are all very readily soluble in water and do not crystallise well; neither the free acid nor the salts can be converted into hexylene oxide by treating with water.

Hexylene oxide boils at 93°, and is soluble in about 15 parts of water at the ordinary temperature. It does not combine with sodium hydrogen sulphite, nor with hydroxylamine in boiling alcoholic solution, and it does not reduce ammoniacal silver nitrate either in alcoholic or aqueous solution. When heated with hydrochloric acid at 140—150°, it yields dichlorhydrin, but it is not converted into the glycol by heating with water at 150—180°. When treated with phosphoric chloride in the cold, it forms resinous products from which no definite compound can be isolated. It combines energetically with bromine, yielding an oily, unstable compound, which is decomposed by water with evolution of heat, and hexylene bromide is precipitated as a heavy oil; the aqueous solution has an acid reaction and reducing properties, and when distilled it gives a distillate free from bromine, which has also reducing properties, and probably contains an aldehyde. When the pseudohexylene glycol described by Würtz is dissolved in well-cooled, concentrated sulphuric acid, it is converted into a hexylene oxide identical with the compound obtained above.

Hydrocarbons of the Allylene Series.—The author's attempts to prepare allylene, $CH_2:C:CH_2$, a gas which has been described by Aarland (*J. pr. Chem.*, 6, 256) and Hartenstein (this Journal, 1873, 1217), were unsuccessful. Allyl iodide and trimethylene bromide were treated with the oxides of sodium, copper, mercury, silver and lead under various conditions, but in no case was allylene formed. When allyl iodide (5 grams) is treated with lead oxide (20 grams) in the cold for 24 hours, a solid, yellow compound seems to be formed; if the mixture is then heated at 130—150° for six hours, propylene (300 c.c.) is obtained. Under the same conditions mercuric oxide forms a red compound with allyl iodide. When allyl alcohol, ethyl allyl ether, or diallyl ether is treated with phosphoric anhydride under various conditions, a gas, probably a mixture of ethylene and propylene, is evolved, but no allylene is formed. (Compare Beilstein and Wiegand, Abstr,, 1885, 740.) α-Epichlorhydrin was treated with sodium under various conditions, and Hartenstein's experiments (*loc. cit.*) with β-epichlorhydrin were repeated, but no allylene was obtained. The bromide (m. p. 195°) described by Hartenstein is possibly hexabromobenzene. Potassium itaconate was submitted to electrolysis as described by Aarland (*loc. cit.*), but only acetylene and a small quantity of a gaseous mixture not absorbable by ammoniacal silver nitrate solution were obtained.

These experiments show that allylene has not yet been isolated, and as the constitution of valerylene is at least doubtful, and the real nature of tetramethylallylene (compare Henry, *Ber.*, 8, 400) has not yet been proved, the author doubts whether any member of the allylene series really exists.

In preparing hydrocarbons of the C_nH_{2n-2} series from the chlorides or bromides, the yield is better, and the reaction is more easily carried out when the bromide is employed. In chlorinating or brominating aldehydes or ketones, which are liable to undergo intramolecular change, by means of phosphoric chloride or bromide, the aldehyde or ketone should be added drop by drop to the chloride or bromide, otherwise the results are very unsatisfactory.

Halogen-derivatives of the formula $C_nH_{2n-1}X$, which easily undergo intramolecular change, are best converted into the unsaturated hydrocarbons by heating with anhydrous potash at 140—150° for 24 to 36 hours.

Alcoholic silver nitrate is the only trustworthy reagent for the higher members of the acetylene series. F. S. K.

Hexyl Iodide from Sorbite. By C. HITZEMANN and B. TOLLENS (*Ber.*, **22**, 1048).—The authors obtained a considerable quantity of crystalline sorbite, $C_6H_{14}O_6 + H_2O$, from the sap of the mountain-ash. When reduced with phosphorus and hydriodic acid, it yields hexyl iodide boiling at about 168°. F. S. K.

Products of the Polymerisation of Ethyl Cyanide. By M. HANRIOT and L. BOUVEAULT (*Compt. rend.*, **108**, 1171—1174).—Sodium in small fragments is dissolved by a solution of ethyl cyanide in anhydrous ether, with evolution of hydrogen and ethane and formation of a white, pulverulent sodium-derivative which alters very rapidly when exposed to the air.

When treated with methyl iodide, the sodium-derivative yields a liquid which on treatment with hydrochloric acid splits up into ammonium chloride and a liquid of the composition $C_7H_{11}NO$, which has a camphoraceous odour and boils at 175°; sp. gr. at 0° = 0·9451, and molecular weight as calculated from the vapour-density = 125.

Ethyl iodide under the same conditions yields a liquid, $C_8H_{13}NO$, which is a higher homologue of the preceding compound and boils at 195°; sp. gr. at 0° = 0·9428, and molecular weight = 139.

If the sodium-derivative is treated with water and then with hydrochloric acid, it yields the lowest homologue, which has previously been obtained in the same way by E. Meyer, who ascribes to it the constitution COEt·CHMe·CN, and states that it boils at 185—191°. The authors find that the true boiling point is 193·5°.

The oxygen in the compounds $C_7H_{11}NO$ and $C_8H_{13}NO$ does not exist in the original product of the action of the alkyl iodide on the sodium-derivative, but is derived from water which has been assimilated under the influence of the hydrochloric acid, thus: $C_6H_8MeN_2H + HCl + H_2O = NH_4Cl + C_6H_8MeNO$. The compound $C_7H_{12}N_2$ has been isolated; it boils at 262°, and after some time forms colourless tabular crystals melting at 43°. This compound, $C_6H_9N_2Me$, must be regarded as derived from the sodium compound $C_6H_9N_2Na$, which is itself produced by the action of an atom of sodium on two molecules of ethyl cyanide.

When the compound $C_7H_{11}NO$ is heated in sealed tubes with hydrochloric acid at 140—150°, it yields carbonic anhydride, ammonium chloride, and ethyl isopropyl ketone boiling at 114°. The compound $C_8H_{13}NO$, under the same conditions, yields ethyl α-butyl ketone boiling at 134—135°. The formation of ammonium chloride shows that the compounds contain the cyanogen-group, which becomes converted into carboxyl, but the liberation of carbonic anhydride shows that the acid which is the immediate product of the reaction splits up into carbonic anhydride and a ketone. This decomposition is characteristic of the α-ketonic acids, and of them alone. It follows that the compounds $C_7H_{11}NO$ and $C_8H_{13}NO$ are α-ketonic nitriles, and have respectively the constitutions $COEt{\cdot}CMe_2{\cdot}CN$ and $COEt{\cdot}CMeEt{\cdot}CN$. The compound $C_7H_{12}N_2$ will consequently be $NH{:}CEt{\cdot}CMe_2{\cdot}CN$, and the sodium-derivative $NH{:}CEt{\cdot}CMeNa{\cdot}CN$.

Ethyl-α-cyanethyl ketone, $COEt{\cdot}CHMe{\cdot}CN$, differs from its higher homologues in that an atom of hydrogen intervenes between the cyanogen-group and the carboxyl-group, this hydrogen being substituted in the higher homologues. It is the nitrile of an acid homologous with acetylacetic acid. It combines with aniline, α-naphthylamine, and phenylhydrazine, with elimination of water and formation of very stable compounds which are under investigation. The higher homologues combine with the first two bases, and with phenylhydrazine they form compounds which decompose spontaneously, and cannot be distilled. C. H. B.

Action of Zinc Chloride on Isobutyl Alcohol in Presence of Hydrochloric Acid. By H. MALBOT and L. GENTIL (*Compt. rend.*, **108**, 957—960).—The action of hydrogen chloride on isobutyl alcohol in presence of zinc chloride yields very little isobutyl chloride, but a large quantity of polybutylenes. The reaction proceeds slowly with isobutyl alcohol and zinc chloride alone, but becomes very rapid, and, finally, even explosive, in presence of hydrogen chloride. The explosive phase was always observed whether the isobutyl alcohol was previously saturated with hydrogen chloride or not. Attempts to reproduce it by using a high temperature and large quantities of zinc chloride were unsuccessful.

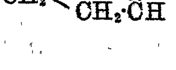
Isobutyl alcohol with hydrogen chloride alone yields only about 3·5 per cent. of isobutyl chloride. If isobutyl chloride is added to a mixture of isobutyl alcohol and zinc chloride, the reaction at once enters the explosive phase, its violence increasing with the proportion of isobutyl chloride added. It is evident that isobutyl chloride plays a very important part in the reaction, and the slow rate of change when isobutyl alcohol is mixed with zinc chloride or hydrogen chloride only is due to the fact that under these conditions only a very small quantity of isobutyl chloride is formed.

The degree of hydration of zinc chloride and the proportion of isobutyl chloride affects the duration of the reaction and the proportion of the products, which are trimethyl methane, isobutylene, polyisobutylenes, trimethylcarbin chloride, isobutyl chloride, and chlorides of the lower polybutylenes. The proportion of the chlorides is small if a small proportion of isobutyl chloride is present, but increases when the liquid is treated with a current of hydrogen chloride.

The separation of the polyisobutylenes by fractionation is very difficult, although their boiling points are widely separated. Amongst those isolated are di-isobutylene boiling at 110—113° under a pressure of 768 mm., and tri-isobutylene boiling at 178—181° under the same pressure. The action of chlorine in the dark at 12° yields amongst other products *chlorodibutylene dichloride*, $C_8H_{15}Cl,Cl_2$, and *dichlorotributylene dichloride*, $C_{12}H_{22}Cl_2,Cl_2$. The nature of the product can be controlled with considerable accuracy by regulating the duration of the action of the chlorine. The vapour-density of di-isobutylene is 3·86; calc., 3·88; that of tri-isobutylene was found to be 2·94, which is only half the calculated value, 5·82. The heat of combustion of di-isobutylene in the calorimetric bomb is 1252·5 Cal., and its heat of formation 51·5 Cal.; the corresponding values for the tri-isobutylene are 1858·9 Cal. and 97·1 Cal. It will be observed that the heats of formation are relatively high. C. H. B.

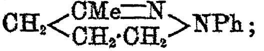
Normal Acetopropyl Alcohol. By A. Lipp (*Ber.*, **22**, 1196—1211; compare Freer and Perkin, Trans., 1887, 702, and 1888, 190).—Acetopropyl alcohol can be prepared by gradually adding a solution of sodium (12 grams) in alcohol (130 grams) to well-cooled ethyl acetate (65 grams), then adding ethylene bromide (94 grams), and heating for 7—8 hours. The alcohol is distilled, the residue mixed with water, the separated oil (65—70 grams), which consists of ethylene bromide, ethyl bromethylacetoacetate, and ethyl diacetoadipate, washed with dilute potash and then boiled for 4 to 5 hours with water (100 c.c.) and hydrochloric acid of sp. gr. 1·10 (20 grams). The solution is separated from the undissolved ethyl diacetoadipate and ethylene bromide, saturated with potassium carbonate, and the acetopropyl alcohol, which separates as an oil, shaken with potassium carbonate and heated at 130° to free it from alcohol; the residue is kept for some days to allow the dissolved potassium carbonate to deposit, and then fractionated under diminished pressure. The yield is 20 per cent. of the theoretical quantity.

Acetopropyl alcohol boils at 207—208° under 729 mm. pressure, with partial decomposition, but it distils undecomposed under reduced pressure (110—160 mm.). It is a colourless, mobile oil, readily soluble in water, alcohol, and ether, and volatile with steam.

The *anhydride*, C_5H_8O, can be obtained by distilling the alcohol very slowly, collecting the distillate over freshly ignited potassium carbonate, warming for a short time with constant shaking, and then distilling the supernatant oil. The yield is small, as most of the alcohol is converted into a thick, oily liquid. It is a very volatile, mobile liquid, boils at 72—75°, and is very unstable, as it seems to be oxidised on exposure to the air. The freshly prepared anhydride dissolves slowly but completely in water, and is reconverted into the alcohol, but after it has been kept for some time it is only partially soluble, and a white, flocculent substance separates from the solution. It combines with phenylhydrazine with evolution of heat, and its vapour imparts a red coloration to a pine-chip moistened with hydrochloric acid. Its constitution is probably  $CH_2<\begin{matrix}O\text{—}CMe\\ \quad\| \\ CH_2\cdot CH\end{matrix}$ (dihydromethylfurfuran).

Acetopropyl alcohol combines with a concentrated aqueous solution of sodium hydrogen sulphite with evolution of heat; if the aqueous solution is allowed to evaporate, crystals separate, and after recrystallising from alcohol the compound $C_5H_{10}O_2,NaHSO_3 + 1\frac{1}{2}H_2O$ is obtained in a pure state. It is readily soluble in water and alcohol, loses its water when kept over sulphuric acid, and is decomposed when warmed with a concentrated solution of potassium carbonate.

Acetopropyl alcohol combines with phenylhydrazine with evolution of heat, and even in dilute solutions phenylhydrazine acetate produces a turbidity. The pure compound $C_{11}H_{14}N_2$ can be obtained by precipitating an aqueous solution of the alcohol with phenylhydrazine acetate, washing the oil with dilute acetic acid, dissolving in ether, and drying the solution over potassium carbonate. It is a reddish-brown oil, almost insoluble in water and dilute acetic acid, and only moderately so in alcohol, but readily in ether, strong acetic acid, and mineral acids. It dissolves in concentrated sulphuric acid with a dark green coloration, and decomposes on exposure to the air. This compound is the anhydride of phenylhydrazinelevulinic acid (compare Fischer, *Annalen*, **236**, 147), and has the constitution



$$\mathrm{CH_2}{<}\substack{\mathrm{CMe{=}N}\\ \mathrm{CH_2\cdot CH_2}}{>}\mathrm{NPh}$$

; when distilled it yields a strong base.

Acetopropyl alcohol is readily reduced by sodium amalgam, and is converted into γ-pentylene glycol; when gently warmed with potassium dichromate and sulphuric acid it is rapidly oxidised to levulinic acid, a considerable rise of temperature taking place.

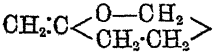
Acetopropyl acetate, $C_5H_9O\cdot OAc$, prepared by boiling the alcohol with acetic anhydride, is a colourless, mobile liquid boiling at 213—214° (728 mm., thermometer entirely in vapour). It is readily soluble in alcohol and ether, and moderately so in water, from which it separates unchanged on adding potassium carbonate. It combines with a concentrated solution of sodium hydrogen sulphite, forming a crystalline compound soluble in water and alcohol. In aqueous solutions, phenylhydrazine acetate produces an oily precipitate.

Acetopropyl benzoate, $C_5H_9O\cdot OBz$, prepared by heating the alcohol with benzoic chloride at 100°, is a thick, colourless liquid boiling at 296—298° with decomposition.

Bromopropyl methyl ketone, $COMe\cdot CH_2\cdot CH_2\cdot CH_2Br$, was obtained in an impure state by dissolving acetopropyl alcohol in hydrobromic acid saturated at 0°, keeping for half an hour, pouring the solution into well-cooled water, and extracting the bromide with ether. After drying and evaporating the ethereal solution, there remains a dark oil which boils at 188—190° with partial decomposition. It boils at 105—106° (60 mm., thermometer entirely in the vapour) seemingly without decomposition, and the distillate is a colourless oil which, however, gradually darkens. It is sparingly soluble in cold water, by which it is slowly decomposed, but when warmed with water it dissolves freely, and is converted into acetopropyl alcohol. It combines with sodium hydrogen sulphite, forming a crystalline compound.

The compound C_5H_8O is formed when bromopropyl methyl ketone is treated with solid potash; it is a mobile oil boiling at 110—111°

(718 mm.), and is moderately soluble in water. When heated for an hour at 100° with 5 per cent. hydrochloric acid it is converted into acetopropyl alcohol, and when treated with phenylhydrazine, combination takes place with evolution of heat, and an oily compound, identical with the phenylhydrazine-derivative of acetopropyl alcohol, is obtained. These experiments show that it has the constitution



$CH_2{:}C<\begin{matrix}O—CH_2\\CH_2{\cdot}CH_2\end{matrix}>$ (trihydromethylenefurfuran); it is therefore isomeric with the anhydride described above, and is very probably identical with the acetyltrimethylene (b. p. 112—113°) obtained by Perkin (Abstr., 1884, 1154) from acetyltrimethylenecarboxylic acid.

F. S. K.

Action of Borax on Polyhydric Alcohols. By L. LAMBERT (*Compt. rend.*, **108**, 1016—1017).—The author confirms Klein's statement that when mannitol, glycerol, erythrol, dextrose, levulose, or galactose, is mixed with a small quantity of boric acid or a biborate, the solution is strongly acid and decomposes carbonates, whilst polyglucosides and quercitol have no such action on borax. He also finds that ethylene glycol, arabite, arabinose, dulcitol, mannitol, and probably sorbite, form similar acid solutions, but inosite, like quercitol, does not. According to Maquenne, inosite and quercitol have a structure different from that of other alcohols, they contain a closed carbon-chain, but have no primary alcoholic function, whilst all the other compounds mentioned have at least one primary alcoholic function. It may, therefore, be stated as a general result, that polyhydric alcohols which contain a primary alcoholic function, and these only, combine with boric acid to form energetic conjugated acids, which decompose carbonates, but are dissociated in dilute solutions. Polyglucosides, such as saccharose and lactose, contain no primary alcoholic group, and would seem to have a constitution similar to that of quercitol and inosite, which probably contain closed carbon-chains (see further, p. 864).

C. H. B.

Action of Chloral on Glucose. By A. HEFFTER (*Ber.*, **22**, 1050—1051).—Two compounds, having the composition $C_8H_{11}O_6Cl_3$, are formed when glucose is heated at 100° for 1 to 2 hours with chloral. The crude product is dissolved in hot alcohol, the solution diluted with a large quantity of hot water to precipitate resinous substances, the filtrate repeatedly evaporated to free it from alcohol and chloral, and the residue fractionally recrystallised from water.

One of the compounds is insoluble in cold water, and separates in thin, tasteless, waxy, anhydrous plates; it melts at 230°, and is readily soluble in hot alcohol, ether and glacial acetic acid, but only sparingly in hot water.

The other compound is sparingly soluble in cold water, and crystallises in colourless, anhydrous needles melting at 186°; it has a bitter taste, and is very readily soluble in alcohol, ether, and glacial acetic acid, but only moderately so in hot water.

Both compounds are dextrorotatory, and reduce Fehling's solution, but they do not reduce mercuric oxide. The more sparingly soluble compound has a distinctly poisonous action, and is not acted on by hot concentrated nitric acid. The more readily soluble compound has no poisonous properties, and is decomposed by concentrated nitric acid, yielding a yellowish oil. Both are oxidised by potassium permanganate in alkaline solution, yielding crystalline acids, containing 36·1 and 36·3 per cent. of chlorine respectively, both of which separate from water in colourless needles, and are very similar in properties; the acid from the more sparingly soluble compound melts at 200—201°, the other at 215°. They both reduce Fehling's solution, and the barium, calcium, copper, and silver salts of both are microcrystalline, and very sparingly soluble or insoluble in water.

F. S. K.

Solubility of Sugar in Water. By L. PÉRIER (*Compt. rend.*, **108**, 1202—1204).—Every specimen of crystallised sugar has it own special coefficient of solubility, but with all specimens, at a given temperature, the solution of each additional gram in 100 c.c. increases the specific gravity by a constant amount for all concentrations between 1 per cent. and 40 per cent. Above 45 per cent. the increase is somewhat less regular, the difference between two consecutive terms gradually becoming smaller. It is, however, easy to construct tables from 1 per cent. to 40 per cent., and from 55 to 100, by taking in each series terms which are not far removed from one another.

The strength of the solution can be calculated from the sp. gr. and *vice versâ*, and the result is accurate to the third decimal place. The calculation is based on the sp. gr. of a 10 per cent. or 50 per cent. solution. If S_{10} is the sp. gr. of a 10 per cent. solution, W the percentage strength of the solution in question, and S_x the required sp. gr.,

$$\frac{S_{10} - 1}{10} \times W = Sx - 1.$$

The reverse operation gives the percentage strength from the sp. gr.

When sugar is rapidly dissolved, especially with sugar-candy, there is a notable development of heat, which cannot be attributed to the formation of hydrates, and is probably due to internal friction.

Glucose behaves in the same way as saccharose, and hence the sp. gr. may be used with advantage for determining the strength of its solutions.

C. H. B.

Compounds of Raffinose with Bases. By A. BEYTHIEN and B. TOLLENS (*Ber.*, **22**, 1047).—Raffinose, like cane-sugar, forms with bases compounds some of which are more sparingly soluble in water and alcohol than raffinose itself.

Di-strontia raffinose, $C_{18}H_{32}O_{16},2SrO$, is prepared by boiling concentrated aqueous solutions of its constituents, but the formation takes place more quickly in presence of alcohol.

Soda raffinosates can be prepared, containing 7 to 8 per cent. or smaller quantities of sodium, according to the quantity of soda employed. 8 per cent. of sodium corresponds fairly well with a di-soda raffinosate, and agrees with the formula $C_{18}H_{32}O_{16} + 5H_2O$ for raffinose.

Other compounds with baryta, lime, and lead oxide have also been prepared. F. S. K.

Xylose and Wood-gum. By H. J. WHEELER and B. TOLLENS (*Ber.*, **22**, 1046).—Wood-gum having all the properties assigned to it by Thomsen, can be obtained from beech-wood and also, but in smaller quantities, from deal, by extracting the wood with 5 per cent. soda, and precipitating the solution with alcohol and hydrochloric acid. When the wood-gum from either source is hydrolysed, it yields Koch's wood-sugar, or xylose.

Xylose closely resembles arabinose in all its properties, and, like the latter, is dextrorotatory; when treated with acids, it yields considerable quantities of furfuramide, but no levulose. The phenylosazone has the composition $C_{17}H_{20}N_4O_3$, so that xylose is a pentaglucose, $C_5H_{10}O_5$, a result which agrees with molecular weight determinations by Raoult's method. When treated with nitric acid it is converted into acids containing 4 or 5 atoms of carbon.

Xylose can also be obtained by the direct hydrolysis of jute.

Xylose and arabinose, and all substances from which they can be obtained, give the cherry-red coloration of arabin when warmed with phloroglucinol and hydrochloric acid. This reaction can be employed for the detection of xylose and arabinose.

Compounds very similar to the hydrazone of mannitol are obtained when wood extract is precipitated with phenylhydrazine.

F. S. K.

Colloïdal Cellulose. By C. E. GUIGNET (*Compt. rend.*, **108**, 1258—1259).—Filter-paper previously treated with hydrochloric and hydrofluoric acids, or carded cotton of the finest quality, is carefully dried and immersed in sulphuric acid of 50° B., care being taken to avoid a rise of temperature. The cellulose forms a transparent, gelatinous mass, which is not affected by contact with a large excess of acid, but is rapidly converted into dextrin at 100°. When the acid has been completely removed by washing, the colloïdal cellulose dissolves in pure water. In order to ensure complete removal of the acid, it is advisable to finish the washing with alcohol, and it is then dried at the lowest possible temperature.

Colloïdal cellulose forms with water a slightly milky solution, which is readily filtered, deposits no precipitate even after several hours, and is not affected by boiling. It has an orange-yellow colour, and is slightly dextrogyrate. Like all colloïds it is precipitated from solution by very small quantities of sulphuric or nitric acid, sodium chloride or sulphate, lead acetate, &c. Alcohol in sufficient quantity produces the same result. Colloïdal cellulose does not reduce Fehling's solution, gives no coloration with iodine, and differs from the achrodextrins in being precipitated by small quantities of salts. If a solution is dried on marble which has been rubbed with vaseline and well polished, it forms brilliant, semi-transparent pellicules, which swell up slightly in water and then dissolve. If immersed in sulphuric acid of 60° for a short time, or in acid of 55° for a longer time, it becomes insoluble in water, and at the same time a small quantity of dextrin is formed. When treated with nitric acid it forms nitrocellulose in the same way as ordinary cellulose, and becomes slightly less transparent.

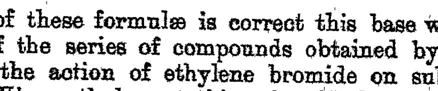
Thin parchment-paper, which has probably been prepared with a somewhat weak acid, yields colloïdal cellulose to boiling water, but thicker paper, which has been treated with stronger acid, is insoluble. Parchment-paper may, in fact, be regarded as a cellular tissue, the pores of which have been filled up with colloïdal cellulose.

C. H. B.

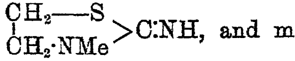
Bromethylamine and its Derivatives. By S. GABRIEL (*Ber.*, **22**, 1139—1154).—When bromethylamine hydrobromide is treated with a cold solution of potash and the resultant oil shaken out with benzene, a solution of the free base is obtained. On evaporation an oil is left which, when exposed to the air, soon solidifies owing to the formation of a carbonate. When the solution of the base is treated with methyl bromide, trimethylbromethylammonium iodide is formed. When bromethylamine hydrobromide is heated with potassium thiocyanate in aqueous solution, it yields a compound, $C_3H_7N_2SBr$, which crystallises in colourless needles, easily soluble in water and melting at 172·5—173·5°. This compound is not bromethylamine thiocyanate or bromethylthiocarbamide (although isomeric with them), but the hydrobromide of a new base. Concentrated potash liberates the *base* $C_3H_6N_2S$, which is soluble in water, alcohol, chloroform, and boiling benzene, crystallises in needles and melts at 84—85°. It is a strong base, its solution colours litmus blue, and may be titrated. The *hydrochloride* crystallises in colourless, flat prisms melting at 198—199°; the *picrate* forms sparingly soluble needles melting at 235°; the *aurochloride* and *platinochloride* sparingly soluble crystals of an orange-yellow and citron-yellow colour respectively. The free base decomposes on distillation, but evaporates slowly on the water-bath. Strong hydrobromic acid at 200° partially decomposes it with evolution of carbonic anhydride and hydrogen sulphide. The base is isomeric with Hofmann's ethylenethiocarbamide (m. p. 194°), and the author therefore proposes for it the name *ethylenepseudothiocarbamide.* When oxidised with bromine-water, it yields Salkowski's taurocarbamic acid,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H.$$

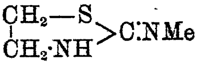
Taking its mode of formation and its reactions into consideration, this base has probably either the constitution—



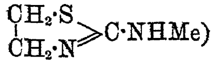
$$\left.\begin{matrix} CH_2\text{—}S \\ | \\ CH_2{\cdot}NH \end{matrix}\right> C{:}NH \quad \text{or} \quad \left.\begin{matrix} CH_2{\cdot}S \\ | \\ CH_2{\cdot}N \end{matrix}\right> C{\cdot}NH_2.$$

If the first of these formulæ is correct this base would form the first number of the series of compounds obtained by Will (Abstr., 1882, 723) by the action of ethylene bromide on substituted thiocarbamides. When ethylene-ψ-thiocarbamide is heated with methyl iodide in methyl alcohol solution, the *methiodide*, $C_3H_6N_2S,MeI$, is obtained. This forms colourless crystals which melt at 159—160°, and are soluble in alcohol and water. When this methiodide is treated with potash it yields *ethylene-ψ-methylthiocarbamide*, $C_4H_8N_2S$, as a colourless oil. The *picrate* forms needles melting at 200—203°: the *platinochloride* and *aurochloride* form long needles soluble in boiling water. When oxidised with bromine-water this methylated base yields Dittrich's methyltaurine, $NHMe\cdot CH_2\cdot CH_2\cdot SO_3H$; it probably therefore has the constitution  $\left.\begin{array}{l}CH_2—S\\ CH_2\cdot NMe\end{array}\right>C{:}NH$, and may also be looked upon as *ν-methyl-μ-imidothiazolidine.*

When bromethylamine is treated with ethyl thiocyanate, *methylethylene-ψ-thiocarbamide,*

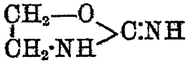


$$\left.\begin{array}{l}CH_2—S\\ CH_2\cdot NH\end{array}\right>C{:}NMe \quad \left(\text{or } \left.\begin{array}{l}CH_2\cdot S\\ CH_2\cdot N\end{array}\right\geqslant C\cdot NHMe\right),$$

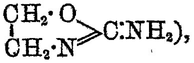


isomeric with the methyl base just described, is formed. It yields glistening needles melting at 90°, and easily soluble in water and the usual solvents. It is strongly alkaline, and gives a *picrate* melting at 224—226°, an *aurochloride*, and a *platinochloride*, all crystallising in needles. When oxidised with bromine-water, it yields an acid which could not be obtained in a pure state, but probably was methyltaurocarbamic acid. This acid when digested with fuming hydrochloride at 150—160° yields carbonic anhydride, methylamine, and taurine. Besides methyl-ψ-ethylenethiocarbamide a compound, $C_8H_{11}N_3S_2$, is formed which melts at 55—60°, is soluble in alcohol, ether, and chloroform, and crystallises in needles. It appears to be a compound of methylethylene-ψ-carbamide and ethyl thiocyanate. The author has obtained the same substance, but in a purer state (m. p. 70°), by acting on methylethylene-ψ-carbamide with ethyl thiocyanate in the cold.

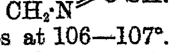
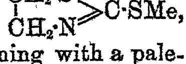
When bromethyleneamine hydrobromide is heated with potassium cyanate *ethylenepseudocarbamide,*



$$\left.\begin{array}{l}CH_2—O\\ CH_2\cdot NH\end{array}\right>C{:}NH \quad \left(\text{or } \left.\begin{array}{l}CH_2\cdot O\\ CH_2\cdot N\end{array}\right\geqslant C{:}NH_2\right),$$



is formed. This was obtained as an oil, but was not pure. The *hydrobromide* crystallises in needles: the *picrate* forms long, yellow needles, soluble in boiling water, and melting at 186—188°. The *aurochloride* yields orange-yellow needles; the *platinochloride* microscopic needles, easily soluble in water.

Bromethyleneamine yields with carbon disulphide bromethylenedithiocarbamic acid, $CH_2Br\cdot CH_2\cdot NH\cdot CS\cdot SH$, which at once loses hydrobromic acid and forms *μ-mercaptothiazoline,*  $\left.\begin{array}{l}CH_2\cdot S\\ CH_2\cdot N\end{array}\right\geqslant C\cdot SH$. This is easily soluble in the fixed alkalis, and melts at 106—107°. Bromine-water oxidises it to taurine. This thiazoline has strongly marked acid properties, and forms metallic salts. When treated with potash and methyl iodide it yields the *methyl ether,*  $\left.\begin{array}{l}CH_2\cdot S\\ CH_2\cdot N\end{array}\right\geqslant C\cdot SMe$, as a colourless liquid boiling at 216—217°, and burning with a pale-blue flame. This ether has a sweetish odour, resembling quinoline, and differs from the parent compound in having basic properties, and being soluble in acids. It forms a *picrate*, an *aurochloride*, and a *platinochloride* as crystalline salts. When oxidised with bromine-water it yields taurine and methylsulphonic acid. L. T. T.

Preparation of Acetylacetone and its Homologues. By L. CLAISEN and E. F. EHRHARDT (*Ber.*, **22**, 1009—1019).—Acetylacetone can be prepared by gradually adding a solution of acetone (75 c.c.) in ethyl acetate (100 c.c.), to a boiling mixture of ethyl acetate (250 c.c.), and finely divided sodium ethoxide (70 grams), boiling for an hour, and pouring the cold mixture into ice-cold water (about 500 c.c.). After separating the supernatant ethyl acetate and neutral condensation-products, the solution is acidified with acetic acid, mixed with a saturated solution of copper acetate (100 grams), and the precipitated copper compound separated by filtration. The yield of the latter is 30—40 grams. A simpler method is to treat a solution of acetone (5·8 parts) in ethyl acetate (30—35 parts) with fine sodium wire (2·3 parts), and, after keeping at the ordinary temperature until most of the sodium has dissolved, heating for a short time on the water-bath. The product is isolated as described above. The yield of acetylacetone is 50—60 per cent. of the acetone employed. The diketone is obtained from the copper compound (compare Combes, Abstr., 1888, 128) by mixing the latter with water and ether, adding dilute sulphuric acid with constant shaking until the salt is entirely dissolved, and extracting the solution with ether. 100 grams of the copper-derivative yield, as a rule, 60—65 grams of acetylacetone.

Acetylmesityl oxide (*acetylangelicylmethane*),

$$COMe\cdot CH_2\cdot CO\cdot CH{:}CMe_2,$$

is formed in the preparation of acetylacetone by either of the methods described above, and is obtained together with the diketone when the alkaline solution is acidified and extracted with ether. It can also be prepared by treating a mixture of mesityl oxide and ethyl acetate with sodium or sodium ethoxide. It is a colourless oil, boils at 204—206°, and shows all the properties of a β-diketone; it dissolves in aqueous alkalis; alcoholic solutions give a red coloration with ferric chloride, and copper acetate precipitates a crystalline, olive-green copper compound from aqueous alcoholic solutions. The *copper compound*, $(C_8H_{11}O_2)_2Cu$, melts at 123°, and is readily soluble in alcohol, ether, benzene, and light petroleum.

A compound, $C_{12}H_{18}O$, is also formed in the preparation of acetylacetone, together with mesityl oxide and isophorone; it boils at 238—242°, and is probably identical with xylitone, obtained by Pinner (Abstr., 1882, 941) in the preparation of phorone, as it is formed in considerable quantities when phorone is treated with sodium ethoxide in ethereal solution.

The following diketones were prepared by the method described above, but as the higher members, especially acetylmethyl hexyl ketone, are sparingly soluble in alkali, after pouring the crude product into ice-cold water, the solution is acidified with acetic acid before separating the ethyl acetate, and the whole extracted with ether. After evaporating the ether and ethyl acetate the residue is dissolved in dilute alcohol, precipitated with copper acetate, and the copper compound treated as described above.

Acetylpropionylmethane, $COEt{\cdot}CH_2{\cdot}COMe$, is a colourless oil boiling at 158°; sp. gr. = 0·9538 at 15°. The *copper* compound, $(C_6H_9O_2)_2Cu$, crystallises from hot alcohol in slender, blue needles melting at 179°.

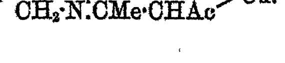
Acetylbutyrylmethane, $COPr{\cdot}CH_2{\cdot}COMe$, prepared as described above, is a colourless oil boiling at 174—175°, sp. gr. = 0·9411 at 15°. This diketone can also be obtained by treating ethyl butyrate with acetone and sodium ethoxide. It is converted principally into acetic acid and butyric acid when boiled with alkalis. The *copper* compound crystallises in blue needles melting at 160—161°. The *azobenzene*-derivative, $COPr{\cdot}CH(N_2Ph){\cdot}COMe$, crystallises in yellow prisms, and melts at 55°.

Acetylheptoylmethane, $C_6H_{13}{\cdot}CO{\cdot}CH_2{\cdot}COMe$, is a liquid boiling at 228—229°. The *copper*-derivative, $(C_{10}H_{17}O_2)_2Cu$, is a blue, crystalline compound melting at 122°.

Acetylpropionylethane, $COMe{\cdot}CHMe{\cdot}COEt$, is formed when diethyl ketone is treated with ethyl acetate under suitable conditions, but it is difficult to separate from the ethyl acetoacetate, which is formed at the same time, as the diketone does not give a precipitate with copper acetate. It is freed from ethyl acetoacetate as completely as possible by fractional distillation, dissolved in aqueous alcohol, treated with an ammoniacal solution of copper oxide, and the blue, crystalline *copper*-derivative, $(C_7H_{11}O_2)_2Cu$ (m. p. 192°), purified by recrystallising from a mixture of benzene and light petroleum. The diketone is a colourless oil boiling at 167—170°.

From a study of the behaviour of various β-diketones, substituted diketones, ketoethereal salts, ethereal salts, and ketoaldehydes towards copper acetate and ammoniacal copper oxide solution, the authors are of the opinion that, as far as their action on the hydrogen of neighbouring methyl- and methylene-groups is concerned, the radicles phenyl, carboxethyl, benzoyl, acetyl, and formyl form a series the first member of which (phenyl) has the least, and the last number (formyl) the most influence.

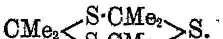
F. S. K.

Action of Diamines on Diketones. By A. COMBES (*Compt. rend.*, **108**, 1252—1254).—Ethylenediamine (2 mols.) acts energetically on acetylacetone (1 mol.) with development of heat and liberation of water, and when the product cools, it forms a white, crystalline mass, which after recrystallisation melts at 111°. It cannot be distilled under ordinary pressure, but boils at about 245° in a vacuum. It has the composition $C_{12}H_{20}N_2O_2$, and most probably the constitution $C_2H_4(N{:}CMe{\cdot}CH_2Ac)_2$, each amido-group in the diamine having reacted with a carboxyl-group. This view is supported by the fact that with copper acetate it yields a beautiful violet precipitate of the composition $C_{12}H_{18}N_2O_2Cu$, almost insoluble in water, but easily soluble in alcohol or chloroform, from which it crystallises in very thin rhomboidal lamellæ melting at 137°. This salt most probably has the constitution 

$$\begin{matrix} CH_2{\cdot}N{:}CMe{\cdot}CHAc \\ | \\ CH_2{\cdot}N{:}CMe{\cdot}CHAc \end{matrix}\!>\!Cu$$

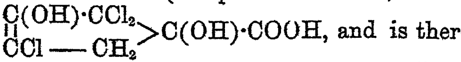
Mineral acids decompose the compound into ethylenediamine and acetylacetone, but the action of dry hydrogen chloride in presence of absolute alcohol yields a crystalline dihydrochloride, $C_{12}H_{20}N_2O_2,2HCl$, melting above 280°.

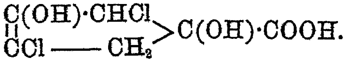
Metacresylenediamine melting at 99° acts on acetylacetone at 100° with elimination of water and formation of a syrupy substance which when heated with sulphuric acid, diluted with water, and saturated with ammonia, yields the compound $C_{12}H_{14}N_2$ in the form of slender, white needles which are quite insoluble in water and melt at 191°. Acetylacetone is formed at the same time. The base, $C_{12}H_{14}N_2$, forms a yellow monohydrochloride and an orange-yellow, crystalline platinochloride, $2C_{12}H_{14}N_2,H_2PtCl_6$. The mercurochloride is pale-yellow, and dissolves in water; the chromate is pale-yellow, and on very slightly heating forms a black, amorphous, insoluble mass similar to that formed by aniline chromate. The base is amidotrimethylquinoline, formed by the action of acetylacetone on one only of the amido-groups in the cresylenediamine. The other amido-group remains unattacked, and yields a diazo-derivative. C. H. B.

Thio-derivatives of Ketones. By E. FROMM and E. BAUMANN (*Ber.*, **22**, 1035—1045).—*Trithioacetone*, $C_9H_{18}S_3$, is obtained when hydrogen sulphide is passed into a well-cooled mixture of acetone and concentrated hydrochloric acid, and is precipitated as a heavy oil on adding water. It solidifies at a low temperature, and can be purified by recrystallising from very cold alcohol, from which it separates in long, colourless needles, melting at 24°, insoluble in water, but readily soluble in ether, chloroform, benzene, and alcohol. It boils at 225—230° with partial decomposition, but it distils undecomposed under greatly reduced pressure (b. p. 130° at 13 mm.). From molecular weight determinations by Raoult's method its molecular formula is $C_9H_{18}S_3$, and its constitution is most probably  $CMe_2{<}{\begin{matrix}S{\cdot}CMe_2\\S{\cdot}CMe_2\end{matrix}}{>}S$. In alcoholic solutions lead acetate produces a bright yellow, and mercuric chloride a colourless precipitate; silver nitrate also gives a colourless precipitate, which, however, rapidly darkens owing to the formation of silver sulphide. When boiled with alkalis, or when heated with phenylhydrazine, it is decomposed with separation of sulphur, but when heated alone for a long time at about 200° it is entirely converted into dithioacetone.

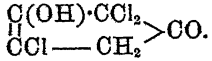
A *sulphone* (*trithioacetone pentoxide*), $C_9H_{18}S_3O_6$, is formed when trithioacetone is oxidised with potassium permanganate in benzene or chloroform solution. It crystallises in needles, softens at 230°, and sublimes when carefully heated, but has no well-defined melting point. It is very sparingly soluble in water, alcohol, ether, and glacial acetic acid, and is very similar in properties to the oxidation product of dithioacetone (compare Autenrieth, Abstr., 1887, 463).

Tetrathiopentone, $C_{15}H_{28}S_4$, is formed, together with other more volatile compounds, in the preparation of trithioacetone, and remains when the crude oil is submitted to fractional distillation. It crystallises from hot alcohol in long, colourless needles, melts at 171°, and is moderately soluble in ether and alcohol, but insoluble in water. The quantity of tetrathiopentone produced depends on the concentration of the hydrochloric acid employed, and the best yield (16 grams) is obtained when anhydrous hydrogen chloride as well as hydrogen sulphide is passed into a well-cooled mixture of acetone (100 grams) and concentrated hydrochloric acid. This compound is also formed when hydrogen sulphide is passed into a well-cooled mixture of acetone and 60—90 per cent. sulphuric acid. F. S. K.

Products of the Action of Chlorine on Phenol in Alkaline Solution. By A. Hantzsch (*Ber.*, 22, 1238—1263; compare Abstr., 1888, 130).—The following experiments prove that the acid $C_6H_5Cl_3O_4$, which is formed by the action of chlorine on phenol in alkaline solution (compare Hantzsch, *loc. cit.*), has the constitution  $\begin{array}{l}C(OH)\cdot CCl_2\\ \|\\ CCl — CH_2\end{array}\!>C(OH)\cdot COOH$, and is therefore a trichlorodihydroxypentenecarboxylic acid. The acid $C_6H_6Cl_2O_4$, obtained from the trichloro-compound by reduction, is analogously constituted, and is a dichlorodihydroxypentenecarboxylic acid,



$$\begin{array}{l}C(OH)\cdot CHCl\\ \|\\ CCl — CH_2\end{array}\!>C(OH)\cdot COOH.$$

When trichlorodihydroxypentenecarboxylic acid or the ammonium salt is carefully warmed with the calculated quantity of chromic acid in aqueous solution, carbonic anhydride is evolved, and on evaporating the ethereal extract, a thick oil remains. This compound cannot be obtained in crystals; it is very readily decomposed by alkalis, even by ammonia, and it gives the reactions for ketones most distinctly. Its constitution is most probably  $\begin{array}{l}C(OH)\cdot CCl_2\\ \|\\ CCl — CH_2\end{array}\!>CO$.

Trichlorodihydroxypentenecarboxylic acid is completely decomposed when treated with bromine in alkaline solution, yielding trihalogen methane-derivatives, but when warmed for an hour at 120° with excess of bromine in aqueous solution, it is converted into carbonic anhydride, oxalic acid, and dichlorotetrabromacetone.

Dichlorotetrabromacetone, $CCl_2Br\cdot CO\cdot CBr_3$, crystallises unchanged from concentrated nitric acid, melts at 80—81°, and is readily soluble in ether and chloroform. It is immediately decomposed when treated with ammonia in aqueous, alcoholic, or ethereal solution, and on adding water (to the alcoholic solution) a compound, $CBr_3\cdot CO\cdot NH_2 + 2CCl_2Br\cdot CO\cdot NH_2$, is precipitated in quadratic plates melting at 130°. This decomposition proves that dichlorotetrabromacetone has the constitution assigned to it above.

Chromic acid converts dichlorodihydroxypentenecarboxylic acid into a ketone-like oxidation product similar to that obtained from the trichloro-acid. Bromine in aqueous solution seems to have the same action as chromic acid when an equivalent quantity only is used, yielding an oil which combines energetically with phenylhydrazine. Dichlorodihydroxypentenecarboxylic acid is decomposed by excess of bromine and water, yielding monochloropentabromacetone; this reaction takes place slowly, even at the ordinary temperature, but it is best to heat at 100° for a short time.

Chloropentabromacetone, $CClBr_2\cdot CO\cdot CBr_3$, crystallises from hot nitric acid and melts at 91—92°. It is decomposed by ammonia, yielding the compound $CBr_3\cdot CO\cdot NH_2 + 4CClBr_2\cdot CO\cdot NH_2$, which melts at 124·5°. All perhalogen acetone-derivatives seem to be decomposed in this way; trichlorotribromacetone, $CCl_2Br\cdot CO\cdot CClBr_2$, for example, yields neither chlorodibromacetone (m. p. 125°) nor dichlorobromacetone (m. p. 139°), but a molecular compound which melts at 133·5°.

Tri- and di-chlorodihydroxypentenecarboxylic acids are decomposed by sulphuric acid with evolution of hydrogen chloride, yielding dichloro- and chloro-diketoamenylcarboxylic acids respectively.

ε-Dichloro-α-δ-diketoamenylcarboxylic acid,

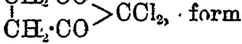
$$COOH\cdot CO\cdot CH{:}CH\cdot CO\cdot CHCl_2,$$

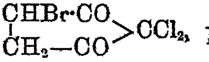
is obtained when pure, finely-divided trichlorodihydroxypentenecarboxylic acid or its ammonium salt is gradually added to a large volume of concentrated sulphuric acid, the solution kept until evolution of hydrogen chloride ceases, then very carefully mixed with well-cooled water, and the whole repeatedly extracted with ether. As the acid is very readily soluble in water, alcohol, ether, &c., it is best purified by pressing on a porous plate and washing with alcoholic benzene, in which it is only sparingly soluble. It separates from water in small, nodular, very hygroscopic crystals, melts at 150—151° with decomposition, and gives a deep red coloration with ferric chloride. It decolorises bromine-water immediately, but the product is very unstable and cannot be isolated. Lead, silver, and mercurous nitrate produce colourless precipitates in neutral aqueous solutions. The *silver* salt, $C_6H_2Cl_2O_4Ag_2$, is a white powder. The *ammonium* salt, $C_6H_4Cl_2O_4 + 2NH_3 + H_2O$, crystallises in quadratic prisms, melts at 106° with decomposition, and is very readily soluble in water but only very sparingly in alcohol.

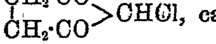
When a solution of phenylhydrazine acetate is added to a moderately concentrated aqueous solution of the acid, a turbidity is produced, and after some time an orange, semi-crystalline tetrahydrazone separates from the solution. This compound, which seems to be formed by the combination of 4 mols. of phenylhydrazine with 1 mol. of the acid, dissolves in alcohol, ether, and benzene with a yellow coloration, but is insoluble in water. It gradually turns brown on exposure to the air, and when heated, is completely decomposed, but without melting. The acid does not combine with orthotoluylenediamine.

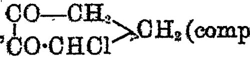
Chlorodiketoamenylcarboxylic acid, $COOH\cdot CO\cdot CH{:}CH\cdot CO\cdot CH_2Cl$, can be prepared by treating dichlorodihydroxypentenecarboxylic acid with concentrated sulphuric acid, and isolating the product exactly as described above, but it can also be obtained by gradually adding zinc-dust to a slightly ammoniacal solution of the dichlorodiketo-acid until no further evolution of heat is perceptible. It crystallises from ether very slowly in small, quadratic prisms, melts at 121° with decomposition, and, in properties, resembles the preceding compound. The *silver* salt has the composition $C_6H_3ClO_4Ag_2 + H_2O$. The *dihydrazone*, $C_{18}H_{17}ClN_4O_2$, is very similar to the tetrahydrazone described above.

When chloro- or dichloro-diketoamenylcarboxylic acid is heated in small quantities at a time, water and hydrogen chloride are evolved, and finally chloro- or dichloro-diketopentamethylene, as the case may be, distils and quickly solidifies. Both these pentamethylene-derivatives are colourless, crystallise very readily, and are readily soluble in warm water and most ordinary solvents, but only sparingly in cold water. They have both a sweet, burning taste and a sweetish, rather phenol-like smell. They react neutral towards litmus, but they form salts from which the original diketo-derivatives are obtained on treating with acids. They are decomposed by warm alkalis or baryta, yielding humus-like substances, and they form dihydrazones with phenylhydrazine, but they do not react with orthodiamines.

Dichlorodiketopentamethylene,  $\left.\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\right>CCl_2$, formed as stated above, crystallises in needles, melts at 118—119°, and sublimes readily, but it cannot be distilled without decomposition taking place. It gives an intense red coloration with ferric chloride and is very stable towards concentrated sulphuric acid. A crystalline, unstable *ammonium* salt is obtained when an ammoniacal solution is evaporated over sulphuric acid. A solution of this salt gives white precipitates with lead, silver, mercurous and mercuric nitrates, a green precipitate with copper salts, and an intense red coloration with ferric chloride. When dichlorodiketopentamethylene is treated with cold concentrated soda, a colourless *sodium* salt, readily soluble in water but sparingly in alkalis, separates from the solution; on warming, complete decomposition ensues. Dichlorodiketopentamethylene is not oxidised by excess of bromine at the ordinary temperature, and only with difficulty by chromic acid, but it is readily decomposed by potassium permanganate, yielding oxalic acid and carbonic anhydride. The *dihydrazone*, $C_5H_4Cl_2(N_2HPh)_2$, is colourless when freshly precipitated, but it soon turns red; it melts at about 84° with partial decomposition.

Bromodichlorodiketopentamethylene,  $\left.\begin{array}{l}CHBr\cdot CO\\ CH_2—CO\end{array}\right>CCl_2$, prepared by treating the dichloro-derivative with bromine and water, crystallises from warm water in shining needles melting at 67°.

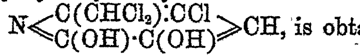
Chlorodiketopentamethylene,  $\left.\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\right>CHCl$, can be obtained in small quantities by reducing the dichloro-derivative with zinc-dust in aqueous solution, but it is best prepared by distilling chlorodiketoamenylcarboxylic acid as described above. It melts at 137°, combines with phenylhydrazine, and is very similar to the dichloro-compound in appearance and properties. Alkaline solutions gradually turn brown, probably the result of oxidation.

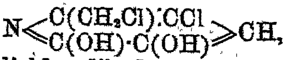
Orthodiketochloropentamethylene,  $\left.\begin{array}{l}CO—CH_2\\ CO\cdot CHCl\end{array}\right>CH_2$ (compare Hantzsch, *loc. cit.*), is much more insoluble and far more unstable than the 1.3-diketone described above. The hydrochloride of the *azine*, $C_{12}H_{11}N_2Cl,HCl + 2H_2O$, is precipitated in a semi-crystalline condition when the yellow sodium salt (*loc. cit.*) is dissolved in water and the solution gradually poured into a dilute hydrochloric acid solution of orthotoluylenediamine, with constant stirring. It is a brownish-red substance, very sparingly soluble in all solvents, and cannot be obtained in a pure condition. F. S. K.

Trichlorodihydroxypentenecarboxylic Acid. By C. HOFFMANN (*Ber.*, **22**, 1263—1270).—Trichlorodihydroxypentenecarboxylic acid (compare preceding Abstract) is best prepared by dissolving phenol (40 grams) in 10 per cent. soda (800 grams), diluting to 1500 c.c., and passing a rapid stream of chlorine through the well-cooled solution until the colour, which at first changes to light-brown and then to black, has finally become a light chocolate-brown, which is generally the case in about 1½ hours. After keeping for an hour, the solution is filtered and the ammonium salt isolated as previously described (Hantzsch, Abstr., 1888, 130). The quantity of ammonium salt obtained is always more than 50 per cent., frequently 66 per cent., and sometimes as much as 100 per cent. of the phenol employed.

Methyl trichlorodihydroxypentenecarboxylate is readily hydrolysed by cold alkalis.

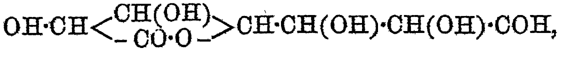
Methyl dichlorodihydroxypentenecarboxylate, $C_5H_5Cl_2O_2{\cdot}COOMe$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from alcohol in rhombic plates, melts at 177—178°, and is readily soluble in alcohol and ether but only sparingly in water; it is quickly hydrolysed by cold alkalis.

Trichlorodihydroxy-α-picoline,  $N{<}\genfrac{}{}{0pt}{}{C(CHCl_2){:}CCl}{C(OH){\cdot}C(OH)}{>}CH$, is obtained when methyl trichlorodihydroxypentenecarboxylate is heated in a sealed tube for 15 minutes, at 80°, with a saturated methyl alcoholic solution of ammonia; the product is evaporated to a syrup and the residue recrystallised from a small quantity of hot water. It forms well-defined, rhombic crystals, containing 4 mols. H_2O, three of which are given off at 70—80°, the remainder only gradually at 130—135°. It melts at 193—194°, is insoluble in ether, and only sparingly soluble in cold water, but more readily in hot water and alcohol. It crystallises unchanged from concentrated hydrochloric or sulphuric acid, it is not acted on by nitrous acid even in boiling aqueous solution, and is only slowly decomposed by boiling alkalis. It has a neutral reaction, but dissolves in soda or ammonia, and the solutions give a white precipitate with silver nitrate, and a greenish-white precipitate with copper sulphate. The *ammonium* salt is crystalline. It does not react with hydroxylamine nor with phenylhydrazine. The *diacetyl*-derivative, $C_6NH_2Cl_3(OAc)_2 + 2H_2O$, prepared by boiling trichlorodihydroxypicoline for a long time with acetic anhydride and precipitating the product with ammonia, crystallises from alcohol, melts at 184—185°, and is almost insoluble in water but soluble in alcohol and ether.

Dichlorodihydroxy-a-picoline,  $N{<}\genfrac{}{}{0pt}{}{C(CH_2Cl){:}CCl}{C(OH){\cdot}C(OH)}{>}CH$, can be obtained by heating methyl dichlorodihydroxypentenecarboxylate at 130° with alcoholic ammonia, but it is best prepared by reducing the preceding compound with sodium amalgam or, better still, with zinc-dust and ammonia. As soon as addition of zinc-dust produces no further evolution of heat, the whole is warmed to 50°, and the filtered solution evaporated. It crystallises in rhombic prisms, melts at 193—194°, and resembles the trichloro-derivative in appearance and properties except that it is much more soluble in water.

Attempts to convert the two chlorodihydroxypicolines into simple pyridine-derivatives were unsuccessful. They are completely decomposed, with evolution of ammonia, when distilled with zinc-dust, but no picoline is formed. When warmed with phosphoric chloride, they yield oils, which are not reconverted into the original compounds by treating with water or alkalis, but a crystalline substance is formed at a higher temperature. This compound (perchlorobutine) is best prepared by heating with excess of phosphoric chloride at 340—350° for 10 hours. It has the composition C_4Cl_6, melts at 32°, boils at 268—269° with slight decomposition, and has probably the constitution $CCl_2{:}CCl{\cdot}CCl{:}CCl_2$. F. S. K.

Aldehydegalactonic Acid. By H. KILIANI (*Ber.*, **22**, 1385—1386).—If, in the preparation of carboxygalactonic acid (this vol., p. 589), the product obtained by oxidising galactosecarboxylic acid with dilute nitric acid is allowed to remain in contact with quicklime for some days instead of being at once evaporated, large, colourless, prismatic crystals of the *lactone* of *aldehydegalactonic acid*,



$$\mathrm{OH{\cdot}CH}<\begin{matrix}\mathrm{CH(OH)}\\ \mathrm{CO{\cdot}O}\end{matrix}>\mathrm{CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}COH},$$

are obtained, the yield amounting to about 10 per cent. of the galactosecarboxylic acid employed. The lactone is readily soluble in hot water, becomes yellow at 190°, and melts with decomposition at 205—206°, reduces an alkaline copper solution, and yields a sparingly soluble hydrazone, $C_{13}H_{16}N_2O_6$, which melts at 166° with decomposition. On oxidation with bromine-water it is converted quantitatively into carboxygalactonic acid. W. P. W.

Preparation of Gluconic Acid. By A. HEFFTER (*Ber.*, **22**, 1049; compare Herzfeld, Abstr., 1888, 807).—*Mercurous gluconate*, $(C_6H_{11}O_7)_2Hg_2$, separates in long, colourless needles when an aqueous (about 10 per cent.) solution of glucose is boiled with yellow mercuric oxide until reduction is complete, and the solution filtered; seemingly no other products are formed in this reaction. This salt is insoluble in alcohol and only sparingly soluble in cold, but readily in hot water. When heated at 100°, it turns grey, and when boiled for a long time with water it is decomposed with separation of mercurous oxide. The free acid can be obtained by decomposing the salt with hydrogen sulphide. The yield is very satisfactory. F. S. K.

Ammonium Malonates. By MASSOL (*Compt. rend.*, **108**, 1060—1061).—The heat of neutralisation of malonic acid by the first equivalent of ammonia is 12·14 Cal., and by the second equivalent, 12·90 Cal.; total 25·94 Cal.

Ammonium hydrogen malonate forms brilliant, colourless, very deliquescent, anhydrous crystals; heat of dissolution at −16° = −6·01 Cal.

$C_3H_4O_4$ solid + NH_3 gas = $C_3H_3O_4NH_4$ solid, develops +22·78 Cal.

The normal malonate readily loses ammonia when its solution is concentrated, as Finkelstein has previously observed. It can be obtained by passing ammonia over the dry ammonium hydrogen malonate, when it forms a white, very deliquescent powder; heat of dissolution at 15° = −2·53 Cal.

$C_3H_4O_4$ solid + $2NH_3$ gas = $C_3H_2O_4(NH_4)_2$ solid.............................. develops +41·015 Cal.

The values for the ammonium malonates are intermediate between those observed with the oxalates and succinates, a result already obtained with the corresponding sodium and potassium salts.

C. H. B.

Oxalo-molybdic Acid and its Salts. By E. PÉCHARD (*Compt. rend.*, **108**, 1052—1055).—Molybdic anhydride dissolves in oxalic acid, forming a syrupy liquid which was mentioned by Berzelius but has not been investigated. If this product is dissolved in dilute nitric acid and allowed to evaporate spontaneously in dry air, it yields large, monoclinic crystals of the composition $H_2C_2O_4,H_2MoO_4$, which dissolve in cold, and more rapidly in hot water, forming a colourless, strongly acid liquid. The dominant faces of the crystals are p and h^3, with the face $b^{\frac{1}{2}}$, the ratios of the axes being $a : b : c = 0·9472 : 1 : 1·0729$, and the angle $ph^1 = 93° 52'$. The formation of crystals is due to the insolubility of the compound in strong nitric acid. The same product is obtained by dissolving the hydrate $MoO_3,2H_2O$ in oxalic acid.

Oxalo-molybdates are formed by direct neutralisation or by double decomposition. The sodium salt is soluble and forms colourless crystals; the silver salt is insoluble in hot water, but dissolves readily in ammonia. The barium salt forms a heavy, white, crystalline precipitate.

Oxalo-molybdic acid is not affected by light when dry, but if moist it becomes blue. Paper moistened with a solution of the acid and dried in the dark, becomes blue on exposure to light. Solutions of the acid remain colourless even in sunlight, and only the walls of the vessel in which it is contained become blue. The blue substance disappears on treatment with water. Paper moistened with a solution of the acid, dried, and heated, becomes black and the colour is not affected by water.

C. H. B.

Ethereal Salts of Cyanomalonic Acid. By A. HALLER (*Ann. Chim. Phys.*, **16**, 403—432).—*Ethyl cyanomalonate*, CN·CH(COOEt)$_2$, can be prepared by passing cyanogen chloride into a cooled alcoholic solution of ethyl sodomalonate. The alcohol is evaporated, the residue treated with water, shaken with ether to remove unchanged ethyl malonate, and the ethereal extract washed with dilute sodium carbonate solution until the washings give no red coloration with ferric salts; the aqueous and sodium carbonate solutions are mixed together, evaporated, acidified with sulphuric acid, and the precipitated oil extracted with ether. The product is then dissolved in sodium carbonate, the filtered solution acidified, the oil washed with water, dried and fractionated under reduced pressure (25 mm.). Ethyl cyanomalonate can also be prepared by treating an alcoholic solution of ethyl sodocyanoacetate with ethyl chlorocarbonate and heating the mixture on the water-bath. It is a colourless oil, boils under reduced pressure (25 mm.) with considerable decomposition, and slowly turns red on exposure to the air. It is only sparingly soluble in water, but more readily in alcohol, ether, and alkalis. It has an acid reaction, decomposes carbonates with evolution of carbonic anhydride, and gives an intense blood-red coloration with ferric salts. The *ammonium-derivative*, $CN\cdot C(NH_4)(COOEt)_2$, crystallises in small prisms and is soluble in alcohol. The *sodium*-derivative, $CN\cdot CNa(COOEt)_2$, is crystalline and readily soluble in water and alcohol. The crystalline *calcium*-derivative ($+2\frac{1}{2}H_2O$) loses its water at 120°, and is more readily soluble in alcohol than in water. The *barium*-derivative ($+4H_2O$) crystallises in long, prismatic needles, readily soluble in alcohol and boiling water; it melts in its water of crystallisation and only becomes anhydrous at about 130°. The *lead*-derivative crystallises in needles and is soluble in alcohol, but only sparingly in water. The *ferric* derivative, $Fe_2[C(CN)(COOEt)_2]_6$, prepared by treating a soluble metallic derivative of ethyl cyanomalonate with a ferric salt, crystallises from ether in red needles, and is soluble in alcohol but insoluble in water.

Methyl cyanomalonate, prepared from methyl sodomalonate and cyanogen chloride as described above, is a reddish oil. The *sodium-derivative*, $CN\cdot CNa(COOMe)_2$, crystallises from water in long needles, and is soluble in water and alcohol; the solutions give a red coloration with ferric salts. The *barium*-derivative,

$$[CN\cdot C(COOMe)_2]_2Ba + 3H_2O,$$

crystallises from alcohol in prisms or quadratic plates.

F. S. K.

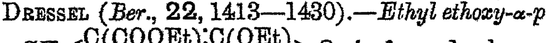
Combination of Normal Magnesium and Lithium Molybdates with Tartaric Acid. By D. GERNEZ (*Compt. rend.*, **108**, 942—945; compare Abstr., 1888, 97 and 938, and 1887, 540).—1·25 grams of tartaric acid was mixed with normal magnesium molybdate in proportions varying from one-twelfth of an equivalent to 5 equivalents, together with sufficient water to bring the bulk of the solution to 50 c.c. at 16°. The rotatory power was measured in a tube 105·7 mm. long, the rotatory power of the tartaric acid alone being 0° 22′. The rotatory power of the mixture increases with the proportion of magnesium molybdate up to 1 equivalent, then again increases at a constant rate, which is 25 per cent. higher than the first rate, up to 1·5 equivalent. Above this point, the effect produced by equal weights of the salt gradually diminishes, and the rotatory power attains its maximum when 2 equivalents of the salt have been added. Any further addition of the molybdate causes a slight reduction in the rotatory power. At first complete combination takes place with formation of the compound $MgMoO_4,2C_4H_6O_6$, and afterwards the compound

$$MgMoO_4,C_4H_6O_6,$$

which has a rotatory power 37·7 times that of the tartaric acid which it contains, and is not materially affected by further quantities of the molybdate.

With lithium molybdate, the phenomena are of precisely the same order. The compound $Li_2MoO_4,2C_4H_6O_6$ is first formed and then the compound $Li_2MoO_4,C_4H_6O_6$, the rotatory power of which is 35 times that of the tartaric acid which it contains.

These results are strictly analogous to those obtained with sodium and ammonium molybdates and with sodium tungstate (*loc. cit.*), and it may be stated as a general result that those compounds of tartaric acid with normal tungstates and molybdates which have a maximum rotatory power consist of equal molecular proportions of the acid and the salt. C. H. B

Ethyl Ethoxy-α-pyronedicarboxylate. By M. GUTHZEIT and O. DRESSEL (*Ber.*, 22, 1413—1430).—*Ethyl ethoxy-α-pyronedicarboxylate*,  $CH{<}^{C(COOEt):C(OEt)}_{C(COOEt)\cdot CO\,—}{>}O$, is formed when ethyl dicarboxyglutaconate in quantities of from 20—30 grams is carefully boiled under a pressure of 15 mm. until the evolution of white vapours has almost ceased and the temperature has risen to about 200°; the contents of the distilling flask are then allowed to cool, and the solid extracted with small quantities of ether to remove the red decomposition products. During the reaction, one molecular proportion of ethyl alcohol is eliminated from the ethyl dicarboxyglutaconate, and the yield of the pyrone-derivative amounts to 70 per cent. of the weight of this compound employed. It is sparingly soluble in cold ether and light petroleum, readily soluble in benzene, acetone, chloroform, and carbon bisulphide, and melts at 94°. As determined by Raoult's method, using benzene as a solvent, its molecular weight is found to be 287·7. It exhibits the properties of a lactone in combining with the elements of alcohol, water, and sodium hydroxide to form derivatives of dicarboxyglutaconic acid, and its relation to γ-pyrone is shown by its conversion into α-pyridone by the action of ammonia.

When boiled with concentrated hydrochloric acid or with aqueous potash in a reflux apparatus, ethyl ethoxy-α-pyronedicarboxylate is converted into glutaconic acid. Ethyl alcohol does not dissolve it appreciably in the cold, but combination ensues with the formation of ethyl dicarboxyglutaconate if the two compounds are allowed to remain in contact for 24 hours. This reaction explains the statement that ethyl dicarboxyglutaconate distils with partial decomposition at 270—280° under the ordinary pressure (Conrad and Guthzeit, *Annalen*, 222, 251), since the products of its decomposition, ethyl alcohol and ethyl ethoxy-α-pyronedicarboxylate, would combine in the receiver with the formation of the apparently unchanged compound. Ethyl ethoxy-α-pyronedicarboxylate also combines with an equimolecular proportion of either normal propyl or normal butyl alcohol, forming salts of dicarboxyglutaconic acid, which, when heated in a vacuum, yield propyl and butyl alcohol respectively, with the formation of ethyl ethoxy-α-pyronedicarboxylate. Ethyl isaconitate (Conrad and Guthzeit, *loc. cit.*) is formed with the evolution of carbonic anhydride when the pyrone-derivative is allowed to remain in contact with water for some weeks, or when it is treated with the calculated quantity of sodium hydroxide in dilute aqueous solution and the resulting yellow solution at once saturated with hydrochloric acid.

Ethyl ethoxy-α-pyronedicarboxylate dissolves in aqueous ammonia, forming a yellow liquid from which hydrochloric acid precipitates a compound having the composition $C_{11}NH_{13}O_6$. This crystallises from ether in slender, matted needles, melts at 155°, is readily soluble in ether, alcohol, and hot water, the solution having an acid reaction, and evolves a distinct pyridine odour when heated with zinc-dust. When boiled with concentrated aqueous soda and the solution precipitated with hydrochloric acid, it is converted into *ethoxy-α-pyridonedicarboxylic acid*, [OH : COOH : COOH : OEt = 2 : 3 : 5 : 6], which crystallises with 1 mol. H_2O in slender needles and melts at 179° with the evolution of carbonic anhydride. W. P. W.

Aconitic Triamide. By E. HOTTER (*Ber.*, **22**, 1077—1079; compare Schneider, Abstr., 1888, 464).—*Aconitic triamide*, $C_6H_9N_3O_3$, is formed when ethyl aconitate (1 part) is kept for a week with very concentrated ammonia. The ethereal salt gradually solidifies to a mass of slender needles, which can be purified by washing with strong ammonia and recrystallising from water. It is insoluble in absolute alcohol, ether, and chloroform, but very readily soluble in hot water, the light yellow solution gradually turning green on exposure to the air. The moist substance becomes green when kept over sulphuric acid, but it can be dried over anhydrous calcium oxide in an atmosphere of ammonia without decomposition taking place. When heated at 250° it turns brown and is completely decomposed at 260°, but without melting. The ammoniacal mother-liquors from the triamide yield, on acidifying, a small quantity of a compound, probably citrazinic acid, insoluble in water; if the ammonia employed in the reaction is not sufficiently concentrated, citrazinic acid alone is formed. F. S. K.

Substitution of the Methylene-hydrogen-atoms in Benzyl Cyanide. By A. ROSSOLYMO (*Ber.*, **22**, 1233—1238; compare Janssen, this vol., p. 596, and Neure, *ibid.*, p. 597).—*Propylbenzyl cyanide*, CHPrPh·CN, can be prepared by boiling benzyl cyanide (1 mol.) for two hours with propyl iodide (1 mol.) and solid caustic soda. The mixture is then treated with benzaldehyde and sodium ethoxide to convert the unchanged benzyl cyanide into phenylcinnamonitrile, from which the product is separated by fractional distillation. It is a colourless liquid boiling at 260—261°.

Propylphenylacetic acid, CHPrPh·COOH, prepared by heating the cyanide at 180—190° with hydrochloric acid, crystallises from light petroleum in small, colourless needles melting at 51—52°.

Benzylpropylbenzyl cyanide, $CH_2Ph{\cdot}CPrPh{\cdot}CN$, prepared by treating propylbenzyl cyanide with benzyl chloride and caustic soda as described above, crystallises from light petroleum in colourless needles, melts at 63° and boils at 330—340°.

Amylbenzyl cyanide, $C_5H_{11}{\cdot}CHPh{\cdot}CN$, is a colourless liquid boiling at 276°.

Benzylamylbenzyl cyanide, $CH_2Ph{\cdot}CPh(CN){\cdot}C_5H_{11}$, separates from alcohol in colourless, nodular crystals melting at 73—74°.

Hexylbenzyl cyanide boils at 287, *heptylbenzyl cyanide* boils at 327°, and *octylbenzyl cyanide* boils at 328°. The last three compounds are yellow oils and do not combine with benzyl chloride. F. S. K.

Alkylene-derivatives of Phenylic Ethers. By L. GATTERMANN, MAISCH, and EHRHARDT (*Ber.*, **22**, 1129—1133).—The authors extended the Friedel-Crafft reaction to syntheses from the chlorides of acid radicles and phenylic ethers, and whilst obtaining the expected ketones (acetoanisoïl, acetophenetoïl, benzanisoïl, and the aceto- and benzo-derivatives of various α- and β-naphthyl ethers were easily prepared) an unexpected reaction was observed. When propionic chloride was heated with anisoïl and aluminium chloride, scarcely any of the expected ketone was obtained, but in place thereof the compound $CHMe{:}C(C_6H_4{\cdot}OMe)_2$. This compound forms silky scales, sparingly soluble in alcohol and melting at 100—101°. The molecular weight, determined by Raoult's method, gave 233 and 242, the formula requiring 254. When heated with an acetic solution of chromic acid, it yields paradimethoxybenzophenone. With hydroxylamine it gives an *oxime* melting at 132—133°. Under like conditions phenetoïl yields the corresponding *ethyl-derivative*, $(C_6H_4{\cdot}OEt)_2{:}C{:}CHMe$, which melts at 76—77°, and in other respects is exactly analogous to the methyl-compound. When bromine-vapour comes in contact with these compounds they at once assume a brilliant violet colour which, however, disappears after about half a minute to reappear on the addition of more bromine-vapour. This alternate coloration and decoloration continues until the whole mass becomes liquid, when it is no longer shown. When bromine is added in acetic acid solution, a transient reddish-violet coloration is formed. The *dibromides*, which are the end result of these reactions, are not coloured. The formation of these compounds is probably explained by the equations :—

$$\text{(i.)}\ C_6H_5{\cdot}OR + CH_2Me{\cdot}COCl = OR{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Me + HCl.$$

$$\text{(ii.)}\ OR{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Me + C_6H_5{\cdot}OR = (C_6H_4{\cdot}OR)_2C{:}CHMe.$$

Whilst with propionic chloride the reaction took place almost entirely in the above direction, with the other acid chlorides it took mainly the normal course. The authors found, however, that small quantities of the corresponding alkylene-derivatives were also formed in these cases. *Ethylidenedimethoxyphenyl*, $CHMe(C_6H_4{\cdot}OMe)_2$, forms micaceous scales melting at 140°, and sparingly soluble in alcohol. The *ethyl*-compound, $CHMe(C_6H_4{\cdot}OEt)_2$, yields micaceous scales melting at 142°.

The abnormal direction of the reaction with propionic chloride is probably due to the impossibility of removing from that compound the last traces of phosphorous chloride, and the authors have found that the addition of a little of this substance determines, with the other acid chlorides, the formation of a much larger proportion of the alkylene-derivative. L. T. T.

Metacresol. By A. CLAUS and A. DREHER (*J. pr. Chem.* [2], **39**, 366—373).—In brominating cresolsulphonic acids, any quantity of bromine less than 3 mols. to 1 mol. of acid produces a dibromocresolsulphonic acid; more than this quantity of bromine yields pure tribromocresol.

Diorthodibromometacresolparasulphonic acid, $C_7H_6Br_2SO_4$ (compare Abstr., 1888, 280) is best obtained as its *potassium salt* (1 mol. H_2O) by dropping a glacial acetic acid solution of bromine (26 grams) into a solution of the potassium parasulphonate (20 grams) in water (600 grams). From this salt, the *barium salt* (1 mol. H_2O) is prepared, and the free acid then obtained by decomposing the barium salt with sulphuric acid. It crystallises in white, lustrous leaflets (1 mol. H_2O), soluble in hot water and sparingly in alcohol. The anhydrous crystals melt at 140° (uncorr.). The *copper* and *cobalt* salt (each with 4 mols. H_2O), the *silver* salt (1 mol. H_2O), *nickel*, and *lead* salts are described. When oxidised, this sulphonic acid yields 2 : 6-dibromotoluquinone (this vol., p. 389), showing that both bromine-atoms are in the ortho-position with regard to the hydroxyl-group.

The authors have obtained the *acid potassium salt* of a second metacresoldisulphonic acid (*loc. cit.*), and are further investigating the matter. When it is treated with bromine, the dibromocresolparasulphonic acid, described above, is obtained; from this fact the authors deduce two formulæ for metacresoldisulphonic acid, in one of which $OH : Me : (SO_3H)_2 = 1 : 3 : 4 : 6$, and in the other $1 : 3 : 2 : 4$.
A. G. B.

Betel-oil. By J. BERTRAM and E. GILDEMEISTER (*J. pr. Chem.* [2], **39**, 349—355).—Eykman obtained a phenol which he called chavicol from the fresh leaves of *Piper betle*, but the authors, who distilled the dried leaves, obtained a phenol differing from this. The leaves yielded 0·5 per cent. of oil, of sp. gr. 1·024 at 15°, containing 70—75 per cent. of a phenol which was isolated by shaking with dilute aqueous soda and decomposing the sodium compound thus formed with sulphuric acid.

Betelphenol, $C_{10}H_{12}O_2$, is a colourless, highly refractive oil of characteristic odour; it boils at 254—255°, and its sp. gr. is 1·067 at 15°. It has the same empirical composition as eugenol, but gives a greener colour with ferric chloride; moreover, pure eugenol boils at 250—251° and has the sp. gr. 1·072 at 15°. The *acetyl-derivative* boils at 275—277° and solidifies about −20°, melting at −5°. The *benzoyl-derivative* crystallises in thin leaflets which melt at 49—50°.

When the acetyl-derivative is oxidised with potassium permanganate an acid is obtained which is isomeric with acetylvanillic acid obtained from the acetyl-derivative of eugenol. *Acetylisovanillic acid*, $C_{10}H_{10}O_5$, crystallises in slender needles or scales, soluble in water and melts at 207°; weak aqueous potash converts it into isovanillic acid. This formation of isovanillic acid points to the formula

$$C_3H_5\cdot C_6H_3(OMe)\cdot OH\ [C_3H_5 : OH : OMe = 1 : 3 : 4]$$

for betelphenol, whilst eugenol is $[C_3H_5 : OMe : OH = 1 : 3 : 4]$, a conclusion which is confirmed by the fact that their methyl-derivatives are identical.

The portion of the betel-oil not affected by alkali distilled for the most part between 250° and 275° as a yellow liquid smelling like tea. When this was dissolved in cooled ether and treated with hydrogen chloride, needle-shaped crystals separated out after some time. The melting point (117—118°) of these is identical with that of a sesquiterpene dihydrochloride, $C_{15}H_{24},2HCl$. which has been obtained in the same way from other oils, such as cubebs and savin. A. G. B.

Action of Borax on Polyhydric Phenols. By A. LAMBERT (*Compt. rend.*, **108**, 1017).—Pyrogallol, catechol, and alkaline tannates and gallates when mixed with borax, yield solutions which are acid to litmus and decompose carbonates. No similar result is obtained with orcinol, quinol, or resorcinol. It is noteworthy that polyhydric phenols capable of forming these acid solutions contain two hydroxyl-groups which occupy contiguous or "ortho-" positions, whilst those which have not this property contain hydroxyl-groups in the meta- or para-position. Catechol, for example, forms an acid solution, whilst resorcinol and quinol do not. C. H. B.

Note by Abstractor.—The thermochemical experiments by Berthelot and Werner (Abstr., 1885, 628) have shown that in the case of polyhydric phenols containing two hydroxyl-groups in the ortho-position, one of these has an alcoholic and not a phenolic function. This is true of pyrogallol and catechol (*loc. cit.*), whilst in resorcinol, quinol, and orcinol both the hydroxyl-groups have phenolic functions. It would seem, therefore, that in all cases the formation of a conjugated acid with borax (see p. 845) is dependent on the presence of an alcoholic function. C. H. B.

Azobenzeneacetoacetamide. By R. LEUCKART and W. HOLTZAPFEL (*Ber.*, **22**, 1406—1408).—*Azobenzeneacetoacetamide*, $C_{16}H_{11}O_2N_3$, is formed by passing a current of ammonia through a well-cooled alcoholic solution of ethyl azobenzeneacetoacetate. It crystallises in bright yellow needles, melts at 144·5°, and is readily soluble in ether and hot alcohol. It is not saponified when heated with aqueous potash, but decomposes with the evolution of ammonia and aniline when fused with potash. Boiling with zinc-dust and dilute potash decomposes it with the evolution of ammonia and formation of aniline and acetic acid. Phenylhydrazine does not react with it unless the two compounds are heated together at 130°; under these conditions ammonia is eliminated and phenylmethylpyrazoloneazobenzene formed. W. P. W.

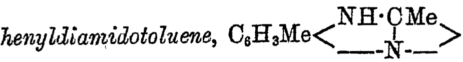
Azoxytoluenes. By J. V. JANOVSKY (*Ber.*, 22, 1172—1176; compare Janovsky and Reimann, this vol., p. 392).—α-Azoxytoluene (m. p. 70°) and β-azoxytoluene (m. p. 75°) both yield paratoluidine, melting at 44—45°, when reduced with tin and fuming hydrochloric acid in warm alcoholic solution. Both compounds have therefore a symmetrical constitution; this fact and their behaviour towards stannous chloride in cold alcoholic solution, a reaction which will be further investigated, proves that their constitution differs from that of azoxybenzene.

α-Bromazoxytoluene is obtained, together with a compound of the formula $C_{28}H_{27}N_4O_2Br$, when α-azoxytoluene (1 mol.) is dissolved in glacial acetic acid and bromine (1 mol.) gradually added to the solution; after keeping for several hours the product is precipitated with water and recrystallised from alcohol. Bromazoxytoluene separates first in yellow, monosymmetric crystals melting at 93°. It is readily soluble in acetone, ether, cold alcohol, and light petroleum, and when reduced with tin and hydrochloric acid it yields paratoluidine and metabromparatoluidine [$NH_2 : Br : Me = 1 : 2 : 4$]. The compound, $C_{28}H_{27}N_4O_2Br$, separates from the alcoholic mother-liquors from the bromazoxytoluene in orange-red crystals melting at 63°.

When β-azoxytoluene is treated with bromine under the same conditions, it yields β-bromazoxytoluene and a compound, $C_{28}H_{27}N_4O_2Br$, identical with that (m. p. 63°) described above. If the glacial acetic acid solution is warmed for a long time, the azoxytoluene is decomposed and a bromo-additive product of azotoluene separates in ruby-red crystals with a green lustre; this compound is decomposed on exposure to the air, with liberation of bromine, yielding parazotoluene. β-Bromazoxytoluene crystallises in flat, yellow prisms, melts at 88°, and is readily soluble in ether, acetone, and light petroleum, but only sparingly in alcohol. When reduced with tin and hydrochloric acid it yields a hydrochloride melting at 202—203°, probably orthobromoparatoluidine hydrochloride, but the base could not be obtained in a solid state.

Nitric acid of sp. gr. 1·4 converts α-azoxytoluene into a mononitrocompound, which crystallises in golden prisms melting at 51°; β-azoxytoluene, on the other hand, yields red needles melting at 82°. Fuming nitric acid converts both α- and β-azoxytoluene into a yellow, crystalline nitro-compound melting at 195—196°. F. S. K.

Reduction Products of Metanitroparacetotoluidide. By Z. BANKIEWICZ (*Ber.*, 22, 1396—1400; compare Abstr., 1888, 1184).—*Azoxyacetamidotoluene*, $C_{18}H_{20}N_2O_3$, is obtained by reducing metanitroparacetotoluidide with excess of ammonium sulphide solution. It crystallises in golden-yellow needles, melts at 196°, and is readily soluble in alcohol and aqueous alkalis, but insoluble in water and dilute acids. In addition to this compound, a small quantity of *azodiacetamidotoluene*, $N_2(C_6H_3Me\cdot NHAc)_2$ [$Me : NHAc : N = 1 : 4 : 3$], is also formed in the reduction with ammonium sulphide; it is, however, best prepared by employing sodium amalgam as the reducing agent. It crystallises in slender, orange-red needles and is sparingly soluble in hot alcohol, insoluble in water, acids, and alkalis.

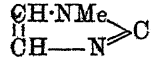
Oxyethenyldiamidotoluene,  $C_6H_3Me{<}\overset{NH\cdot CMe}{\underset{N}{|}}{>}O$, is formed in the reduction of nitroacetotoluidide with ammonium sulphide in the cold, if care is taken to have the latter free from ammonium hydrosulphide and not too concentrated. It crystallises in colourless, anhydrous tables, melts at 232—234° with decomposition, and is soluble in hot alcohol, sparingly soluble in hot water. It is very stable, and undergoes no change when boiled with concentrated hydrochloric acid, stannous chloride and hydrochloric acid, or alkalis. On distillation with zinc-dust it yields ethenyldiamidotoluene (Hobrecker, this Journal, 1875, 173). The *hydrochloride*, $C_9H_{10}N_2O,HCl$, crystallises in colourless prisms; the *platinochloride*, $(C_9H_{10}N_2O)_2,H_2PtCl_6$, crystallises in reddish prisms; the *nitrate* crystallises in needles.

Boesneck's amidoacetotoluidide is also formed in the reduction of nitroacetotoluidide with ammonium sulphide; its *picrate*,

$$NHAc\cdot C_6H_3Me\cdot NH_2,C_6H_2(NO_2)_3\cdot OH,$$

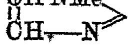
crystallises in stellar aggregates of scales. W. P. W.

Condensation Products of Amidoacetal. By A. WOHL and W. MARCKWALD (*Ber.*, **22**, 1353—1362; compare this vol., p. 624).— Phenylimidazole melts at 13°; it gives with many metallic salts precipitates which are readily soluble in alcohol and dilute acids. The compound obtained with silver nitrate crystallises from dilute alcohol in slender, colourless needles, and has the composition $(C_9H_8N_2)_2,AgNO_3$.

Methylimidazolylmercaptan,  $\overset{CH\cdot NMe}{\underset{CH——N}{\|}}{>}C\cdot SH$, is obtained by treating acetalylamine (1 mol.) with methyl thiocarbimide (1 mol.), and boiling the resulting oily acetalylmethylthiocarbamide,

$$NHMe\cdot CS\cdot NH\cdot CH_2\cdot CH(OEt)_2,$$

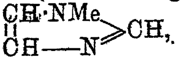
with hydrochloric acid or 30 per cent. sulphuric acid for half an hour. It crystallises from hot alcohol or from a mixture of benzene and chloroform in colourless plates, melts at 141—142°, boils at about 280° with partial decomposition, and is readily soluble in water, moderately so in alcohol and chloroform, but only sparingly in benzene, ether, and light petroleum. The *hydrochloride* can be obtained in crystals by passing hydrogen chloride into a chloroform solution of the base; it is very deliquescent. The *platinochloride*, $(C_4H_6N_2S)_2PtCl_4$, is a red, the *aurochloride*, $C_4H_6N_2S,AuCl_3$, a deep purple, crystalline compound. The *silver* compound, $C_4H_5N_2SAg$, is colourless. Mercuric nitrate produces a white, lead acetate a yellow, and copper sulphate a greyish-blue precipitate. The *methiodide*, $C_4H_6N_2S,MeI$, prepared by treating the mercaptan with methyl iodide in chloroform solution, crystallises in colourless needles, melts at 148°, and is readily soluble in water but only moderately so in alcohol, and insoluble in all other solvents.

Methylimidazolyl methyl sulphide,  $\overset{CH\cdot NMe}{\underset{CH——N}{\|}}{>}C\cdot SMe$, prepared by

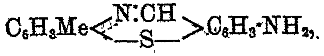
decomposing the methiodide with alkalis, is a colourless, mobile, strongly alkaline liquid boiling at 225° (uncorr.); it is miscible with water, alcohol, and ether, but only sparingly soluble in dilute alkalis. It gives crystalline, reddish-yellow precipitates with platinic and auric chlorides; the *nitrate* is crystalline. The *methiodide* (*sulphinium iodide*), $C_5H_8N_2S,MeI$, crystallises in colourless needles, melts at 173°, and is readily soluble in water and moderately so in alcohol, but insoluble in all other solvents. It is not decomposed by cold alkalis, but on warming, mercaptan is liberated.

The *nitro*-compound, $C_5H_7N_2S\cdot NO_2$, is precipitated in crystals when methylimidazolyl methyl sulphide is boiled with dilute nitric acid, the solution evaporated to a syrup and mixed with water. It crystallises from hot dilute acids in small, yellow needles, melts at 85°, gradually turns red on exposure to the air, and is readily soluble in alcohol, ether, and moderately strong acids, but only sparingly in cold water. The *platinochloride*, $(C_5H_7N_2S\cdot NO_2)_2,H_2PtCl_6$, forms yellow crystals, melts at 197° with decomposition, and is readily soluble in water but only sparingly in alcohol. The *aurochloride* is a yellow, crystalline compound, soluble in alcohol.

The compound (m. p. 115—116°) obtained in like manner from phenylimidazolyl methyl sulphide (*loc. cit.*), and described as a sulphone, is in reality a nitro-compound analogous to the above.

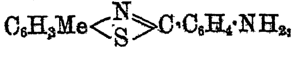
Methylimidazole,  $\left.\begin{array}{l} CH\cdot NMe \\ \| \\ CH\text{——}N \end{array}\right> CH$, prepared by digesting methylimidazolylmercaptan with dilute nitric acid, melts at −5°, boils at 193—194°, and is identical with methylglyoxaline (Wallach., Abstr., 1882, 821). The last-named compound has, therefore, the constitution assigned to it by Japp (Trans., 1883, 1). The *hydrochloride* is crystalline, but very deliquescent. The *nitrate* crystallises from water in colourless prisms. The *picrate*, $C_4H_6N_2,C_6H_3N_3O_7$, crystallises in small, golden needles, melts at 158°, and is sparingly soluble in water, alcohol, and ether. The platinochloride softens at 173—175°, melts at 187° with decomposition, and is moderately soluble (7·02 per cent. at 13°) in water. The *aurochloride*, $C_4H_6N_2,HAuCl_4$, is a yellow, crystalline compound melting at 118—120°. The mercurocyanide crystallises in long, colourless needles, melts at 118°, and is readily soluble in alcohol and moderately so in water. F. S. K.

Constitution of Primuline. By W. PFITZINGER and L. GATTERMANN (*Ber.*, **22**, 1063—1068).—Green (Trans., 1889, 233), has assigned to dehydrothiotoluidine the constitution



$$C_6H_3Me{<}\begin{smallmatrix}N:CH\\ S\end{smallmatrix}{>}C_6H_3\cdot NH_2,$$

but the authors are of opinion that it has the constitution



$$C_6H_3Me{<}\begin{smallmatrix}N\\ S\end{smallmatrix}{>}C\cdot C_6H_4\cdot NH_2,$$

and for the following reasons: When dehydrothiotoluidine is diazotised in boiling alcoholic solution (compare this vol., p. 602) it yields a compound, melting at 122—123°, which has the constitution

$C_6H_3\overset{-}{Me}<\genfrac{}{}{0pt}{}{N}{S}>CPh$, as is proved by the fact that it is identical with the substance obtained from benzoic chloride and parametamidothiocresol. (Compare Hess, Abstr., 1881, 596.) This same compound (m. p. 122—123°) can also be prepared by oxidising thiobenzotoluidide with alkaline potassium ferricyanide solution, so that there is no doubt that it has the above constitution. Moreover, when benzenylamidothiocresol is fused with potash, it is decomposed into benzoic acid and amidothiocresol; the latter was converted into the diazosulphide, and the resulting compound was found to be identical with the substance $C_6H_4Me<\genfrac{}{}{0pt}{}{S}{N}>N$, prepared by Jacobson and Ney (this vol., p. 772). When dehydrothiotoluidine is fused with potash, it yields amidobenzoic acid and amidothiocresol, a decomposition which is in accordance with the author's constitutional formula.

Primuline-base (1 part) was heated with potash (2·5 parts) at 250—270° until the melt was completely soluble in water, the alkaline solution was then strongly acidified with hydrochloric acid and treated with sodium nitrite until the solution gave the starch and potassium iodide reaction. A considerable quantity of a yellow, crystalline compound was precipitated, and the filtrate contained a diazo-compound, which gave a yellowish-red dye with β-naphthol, and was, therefore, an amido-acid, most probably paramidobenzoic acid. The precipitate consisted of a portion soluble in sodium carbonate, most probably phenylenediazosulphidecarboxylic acid, and an insoluble portion which was proved to be the diazosulphide referred to above.

The authors give two possible formulæ for the primuline-base, the constitution of which they are engaged in proving. F. S. K.

History of Primuline. By L. Gattermann and P. Jacobson (*Ber.*, 22, 1372—1374).—A reply to Green (*Ber.*, 22, 968), defending the authors' claim to the right to investigate the nature of dehydrothiotoluidine and primuline. The authors states that in Green's first paper (*J. Soc. Chem. Ind.*, 1888, 179) no mention is made of the source or nature of primuline, except that it is a salt of an amido-acid, and that the method of preparation of dehydrothiotoluidine was made known not by Green but by Dahl & Co., in the German patent No. 35,790 (compare Jacobson, this vol., p. 498; Gattermann, *ibid.*, p. 602; also Green, Trans., 1889, 228). W. P. W.

Substances which form Coloured Compounds with Mordants. By S. v. Kostanecki (*Ber.*, 22, 1347—1353; compare Abstr., 1888, 274; this vol., p. 137).—Nitropyrocatechol $[(OH)_2 : NO_2 = 1 : 2 : 3]$ gives with alumina mordants orange shades similar to those obtained with nitropyrogallol, whereas the isomeric compound forms bright-yellow compounds. The property of forming coloured compounds depends, therefore, in the case of dihydroxy-derivatives, on the relative position of the two hydroxyl-groups, and not on that of the chromophore.

Anthraquinoneoxime [O : NOH = 1 : 4] does not form coloured compounds with mordants; phenanthraquinoneoxime [O : NOH =

1 : 2], on the other hand, forms coloured precipitates with metallic salts. Retenequinoneoxime [O : NOH = 1 : 2] forms green compounds with iron mordants.

Orthonaphthalenedioxime colours iron and cobalt mordants brown, but the isomeric para-compound has no tinctorial properties. Parabenzenedioxime is without action on metallic salts, but benzenetetroxime (adjacent) gives brownish-black compounds with iron mordants.

Orthhydroxyoximes, such as dihydroxyquinonedioxime

$$[(NOH)_2 : (OH)_2 = 1 : 4 : 2 : 5]$$

and hydroxynaphthaquinoneoxime [NOH : OH : O = 1 : 2 : 3] (compare this vol., p. 887), form colouring matters with mordants, but α-nitroso-α-naphthol [O : NOH = 1 : 4] and juglonemonoxime [O : NOH = 1 : 4] have no tinctorial properties.

Many orthhydroxyquinones, for example orthhydroxynaphthaquinone [O_2 : OH = 1 : 4 : 2] and hydroxyjuglone, form slightly coloured compounds with mordants, but the rule is not a general one. Orthhydroxythymoquinone, for instance, and juglone do not dye mordanted materials.

Dihydroxyquinone [$O_2 : (OH)_2$ = 1 : 4 : 2 : 5], chloranilic acid, nitranilic acid, and rhodizonic acid all yield colouring matters with mordants. F. S. K.

The Theory of Dyeing. By E. KNECHT and J. R. APPLEYARD (*Ber.*, **22**, 1120—1125).—The property of a sulphuric acid solution of wool to precipitate intensely coloured lakes from solutions of coal-tar colours (Knecht, this vol., p. 49), is due to the presence of lanuginic acid (this Journal, 1871, 381). The authors have re-examined this substance, which is best obtained by dissolving wool in a strong solution of barium hydroxide and precipitating with lead acetate. Lanuginic acid forms a dirty-yellow, non-deliquescent mass. (The deliquescent character of Champion's acid was probably due to its still containing traces of nitric acid.) At 100° it becomes soft and plastic, and at a higher temperature swells, turns brown, and gives off an odour of burning wool. Champion ascribed the formula $C_{19}H_{30}N_5O_{10}$ to lanuginic acid, but the authors find that it contains 3 per cent. of sulphur. It is soluble in water, sparingly so in alcohol, insoluble in ether. Its solution precipitates colouring matters in the form of intensely coloured lakes, most of which melt below 100°. Tannic and chromic acids, and the oxides of most of the heavy metals, are also precipitated by it. It has the characteristics of a proteïd, does not coagulate, and shows the characteristic reactions with Millon's reagent and with phosphomolybdic acid. Its analysis gives the percentage composition C = 41·63, H = 7·31, N = 16·26, S = 3·35, O = 31·44. The picrate forms a light-yellow powder.

Experiments made to determine the maximum quantities of various dyes taken up by wool gave the following results in percentages of the weight of wool taken:—Picric acid, 13·3 per cent.; naphthol-yellow S, 20·8 per cent.; tartrazine, 22·6 per cent.; crystal-violet, 8·4 per cent. Taking picric acid as the unit, these numbers correspond almost exactly with the molecular proportions $1 : 1 : \frac{3}{4} : \frac{1}{3}$. The authors conclude that when an excess of colouring matter is used, it forms a definite chemical compound with the wool-fibres. The lanuginic acid probably exists in combination in the wool-fibres, and when a mordant is added in the process of dyeing, takes the metallic oxide, whilst the acid of the mordant goes to the basic part of the wool-fibre, and the lanuginate formed then combines with the colouring matter added to produce a coloured lake. L. T. T.

Amidomercaptan. By S. Gabriel (*Ber.*, **22**, 1137—1139).—The best method for the preparation of bromethylphthalimide,

$$C_8H_4O_2{:}N{\cdot}C_2H_4Br,$$

is to mix potassium phthalimide (100 grams) with a large excess of ethylene bromide (300 grams instead of 100 grams) and heat the whole for about seven hours, so that the bromide is kept constantly boiling vigorously, and afterwards to remove the excess of bromide by distilling it off in a current of steam. The yield is then about 73 per cent. of the theoretical.

When bromethylphthalimide and potassium hydrosulphide are heated together under pressure at 100°, *mercaptophthalimide*, $C_6H_4{:}C_2O_2{:}CH_2{\cdot}CH_2{\cdot}SH$, is formed. It is soluble in alcohol, ether, and chloroform, crystallises in colourless scales, and melts at 75—77°. When heated at 200° with concentrated hydrochloric acid, it yields *amidomercaptan hydrochloride*, $SH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2{,}HCl$, which forms colourless crystals melting at 70—72°.

Small quantities of the corresponding disulphide seem also to be formed with the mercaptophthalimide. L. T. T.

Action of Hydroxylamine on Ethereal Salts. By A. Jeanrenaud (*Ber.*, **22**, 1270—1284).—Hydroxamic acids can be conveniently prepared by treating ethereal salts with hydroxylamine in alkaline solution.

Benzhydroxamic acid is best prepared by adding sodium ethoxide (1 mol.) to an alcoholic solution of hydroxylamine hydrochloride (1 mol.), filtering from the precipitated sodium chloride, and treating the filtrate with ethyl benzoate (1 mol.) and sodium ethoxide (1 mol.). Crystals of sodium benzhydroxamate separate from the solution, together with the gelatinous additive compound of ethyl benzoate and sodium ethoxide; after removing the latter by washing the precipitate with alcohol, the residual sodium salt is dissolved in water, decomposed with hydrochloric acid, and the acid recrystallised from alcohol. If the sodium salt is washed carefully, the product contains no dibenzhydroxamic acid, and only traces of benzoic acid. The yield is above 40 per cent. of the theoretical quantity.

Attempts to prepare dihydroxamic acids from ethyl phthalate and ethyl succinate by this method were unsuccessful.

Salicylhydroxamic acid, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}OH$, is obtained by treating methyl salicylate with a slight excess of hydroxylamine hydrochloride and of soda in aqueous solution, and, after several hours, acidifying with hydrochloric acid. Neither potash nor yet too large an excess of soda should be employed. It crystallises in colourless needles, turns reddish on exposure to the air, melts at 169°, and sublimes when carefully heated, but decomposes at a temperature slightly above its melting point. It is sparingly soluble in cold water, but more readily in alcohol, ether, and hot water. Ferric chloride produces in aqueous solutions a reddish precipitate, which dissolves in excess, forming a reddish-violet solution; on adding more ferric chloride, the colour changes to deep-red. This reaction seems to be common to all monohydroxamic acids. Aqueous solutions of the acid impart a reddish coloration to paper and to the skin. In neutral solutions, silver nitrate, lead acetate, mercuric chloride, zinc sulphate, and cadmium sulphate produce colourless, copper and nickel sulphates green precipitates. The *lead* salt, $(C_7H_6O_3N)_2Pb + 4H_2O$, loses its water at 110—115°.

Salicylhydroxamic acid can also be prepared by treating the ethyl or methyl ether of ethyl salicylate with hydroxylamine as described above, but hydroxylamine has no action on salicylic acid nor on ethyl meta- and para-hydroxybenzoate.

α-Hydroxy-β-naphthhydroxamic acid, $OH{\cdot}C_{10}H_6{\cdot}CO{\cdot}NH{\cdot}OH$, is best prepared by treating finely-divided methyl α-naphthol-β-carboxylate with a cold, strongly alkaline solution of hydroxylamine hydrochloride. The solution is kept for some days and shaken frequently, then filtered, the filtrate acidified with hydrochloric acid, and the precipitate again treated with hydroxylamine in alkaline solution; finally, the filtered solution is acidified, extracted with ether, and the acid purified by recrystallising from ether. It is thus obtained in colourless, microscopic crystals, which quickly turn brown; it begins to decompose at 160°, melts at 174°, and is very sparingly soluble in water, but readily in alcohol and ether. It dissolves in alkalis and ammonia, forming green solutions, from which green salts gradually separate. Aqueous solutions give a violet coloration with ferric chloride, and in neutral solutions most metallic salts produce sparingly soluble precipitates.

β-Hydroxy-α-naphthhydroxamic acid is prepared by treating methyl β-naphthol-α-carboxylate with a cold, strongly alkaline solution of hydroxylamine hydrochloride, keeping for 12 hours, after which time solution is complete, precipitating with acids, and treating the precipitate with hydroxylamine in ammoniacal solution. It is a yellow, amorphous compound, melts at 178° with previous decomposition, and is readily soluble in alcohol, but only sparingly in water and ether. Aqueous solutions give a violet coloration with ferric chloride, and in ammoniacal solutions most metallic salts produce precipitates, either immediately or after some time.

Methyl β-naphthol-β-carboxylate does not yield a hydroxamic acid when treated with hydroxylamine as described above or under modified conditions.

Dihydroxyterephthaldihydroxamic acid, $C_6H_2(OH)_2(CO{\cdot}NH{\cdot}OH)_2 + 2H_2O$, is obtained, together with tetrahydrodihydroxyterephthalic acid (see below), when ethyl dihydroxyterephthalate (ethyl quinonehydrodicarboxylate) is dissolved in a quantity of soda exactly sufficient for complete solution, and treated with excess of an aqueous solution of hydroxylamine hydrochloride. The dihydroxyterephthaldihydroxamic acid crystallises from the solution after a short time, and the mother-liquors contain the tetrahydrodihydroxyterephthalic acid, which is precipitated on adding dilute hydrochloric acid. It crystallises in well-defined hexagonal prisms, which lose their water over sulphuric acid, begin to turn brown at 165°, and are completely decomposed at 260°. It is moderately easily soluble in all solvents, and in aqueous solutions ferric chloride produces a bluish-violet coloration, which becomes dark-green on adding excess of the reagent. It forms sparingly soluble salts with many metals; the silver salt is quickly reduced. When warmed with dilute hydrochloric acid, it is quickly converted into quinonehydrodicarboxylic acid, but it is reprecipitated unchanged on adding acids to the alkaline solution.

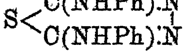
Tetrahydrodihydroxyterephthalic acid, $C_6H_6(OH)_2(COOH)_2$, crystallises in yellowish-brown prisms, begins to decompose at 179°, melts at 189—191° with complete decomposition, and is sparingly soluble in cold water but very readily in alcohol and ether. Aqueous solutions give a brown coloration with ferric chloride, and in neutral solutions most metallic salts produce crystalline precipitates. The *ammonium* salt, $C_6H_6(OH)_2(COONH_4)_2$, crystallises in yellowish needles. The *barium* salt, $C_6H_6(OH)_2(COO)_2Ba$, prepared by precipitating an ammoniacal salt of the acid with barium chloride, is a colourless, microcrystalline powder. The *silver* salt, $C_8H_6O_6Ag_4 + 2H_2O$, crystallises from water in long, colourless needles. The ethyl salt is identical with the ethyl hydroquinonetetrahydrodicarboxylate (m. p. 128°) which was prepared by Hantzsch and Zeckendorf (*Ber.*, **20**, 2801) from the hydrate of ethyl quinonehydrocarboxylate; the acid itself is isomeric with the acid obtained by Hermann by decomposing ethyl succinosuccinate with alkalis in absence of air.

Attempts to prepare a hydroxamic acid from ethyl dichlorohydroquinonedicarboxylate were unsuccessful.

Ethyl quinonedioximecarboxylate, $C_6H_3(NOH)_2 \cdot COOEt$, is formed when ethyl succinosuccinate is dissolved in very dilute soda, mixed with hydroxylamine, and the solution kept for about an hour out of contact with air; on acidifying the well-cooled solution with hydrochloric acid, light-yellow crystals are precipitated. It crystallises from hot water in almost colourless prisms, begins to melt at 160°, and explodes at a higher temperature. It is identical with the compound obtained by Baeyer by treating ethyl succinosuccinate with hydroxylamine in neutral solution, so that ethyl succinosuccinate does not form an oxime. F. S. K.

Action of Hydrogen Peroxide on Phenylthiocarbamide.

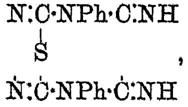
By D. S. Hector (*Ber.*, **22**, 1176—1180).—*Dianilidoorthodiazothiole*,



$S<\begin{matrix}C(NHPh){:}N \\ C(NHPh){:}N\end{matrix}$

, is obtained when phenylthiocarbamide (5 grams), dissolved in hot dilute alcohol and a few drops of hydrochloric acid, is treated with a 3 per cent. solution of hydrogen peroxide (40—50 grams) in small portions at a time. The solution is filtered from the separated sulphur (about 5 grams), neutralised, and the precipitate recrystallised from boiling alcohol, from which it separates in colourless needles. It is readily soluble in glacial acetic acid and hot alcohol, but only very sparingly in cold alcohol and benzene, and insoluble in water; it dissolves readily in mineral acids, but is reprecipitated on adding alkali. When boiled with a solution of silver nitrate, no separation of silver sulphide occurs, but when treated with zinc and hydrochloric acid in alcoholic solution, hydrogen sulphide is evolved, and on adding water an oil is precipitated. The *hydrochloride* and the *sulphate* are very readily soluble in water, and could not be obtained in crystals. The *nitrate*, $C_{14}H_{12}N_4S,HNO_3$, separates from water in nodular crystals. The *platinochloride*, $C_{14}H_{12}N_4S,H_2PtCl_6$, is a crystalline salt, insoluble in water and alcohol. The *dichromate* is insoluble in water and alcohol. The *picrate* separates from alcohol in yellow crystals. The *silver nitrate*-derivative, $C_{14}H_{12}N_4S,AgNO_3 + H_2O$, prepared by boiling an alcoholic solution of the base with silver nitrate, forms small, granular crystals, and is very sparingly soluble in hot alcohol; it decomposes on exposure to light, and explodes when heated. Mercuric chloride also gives a colourless insoluble compound. The *acetyl*-derivative, $C_{14}H_{11}N_4SAc$, prepared by dissolving the base in acetic anhydride, crystallises in shining needles melting at 233°. The *benzoyl*-derivative, $C_{14}H_{11}N_4SBz$, obtained by boiling the base with benzoic chloride, crystallises in colourless plates melting at 238°. The *nitroso*-derivative, $C_{14}H_{11}N_4S\cdot NO$, separates as a green powder when a dilute hydrochloric acid solution of the base (1 mol.) is treated with an aqueous solution of potassium nitrite (1 mol.). It turns yellow when dried, is insoluble in water and alcohol, and explodes when heated.

Dianilidoorthodiazothiole cyanide,



$$\begin{array}{l} N{:}C\cdot NPh\cdot C{:}NH \\ \;| \\ S \\ \;| \\ \dot{N}{:}\dot{C}\cdot NPh\cdot \dot{C}{:}NH \end{array}$$

, separates when cyanogen is passed into a warm alcoholic solution of the base. It crystallises from alcohol, in which it is moderately easily soluble, in moss-like needles, and dissolves in dilute hydrochloric acid, but is reprecipitated on adding alkalis.

F. S. K.

Disalicaldehyde. By W. P. Bradley (*Ber.*, **22**, 1134—1137).—When bromine acts on disalicaldehyde, mono- and di-bromosalicaldehydes are formed together with a dibromodisalicaldehyde, $C_7H_4O_2Br_2$. The latter crystallises in needles, is insoluble in alkali, soluble in a mixture of alcohol and ether, and melts at 165—166°. Monobromosalicaldehyde melts at 104—105°, the lower melting point hitherto given being due to the presence of impurities.

L. T. T.

Cyanacetophenone and its Derivatives: Synthesis of α-Ketonic Acids. By A. Haller (*Compt. rend.*, **108**, 1116—1118).—When an alcoholic solution of cyanacetophenone neutralised with sodium hydroxide is mixed with the theoretical quantity of diazobenzene chloride, and the product is washed and crystallised from alcohol, *azobenzenecyanacetophenone*, $COPh\cdot CH(CN)\cdot N_2\cdot Ph$, is obtained in long, silky, yellow needles, insoluble in cold water, and almost insoluble in cold alcohol, but soluble in boiling alcohol and in alkalis; it melts at 135·7°.

Orthomethylcyanacetophenone, $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}CN$, obtained by the decomposition of ethyl orthotoluylcyanacetate (Abstr., 1888, 1298), crystallises in modified rhombic prisms which melt at 74·4°, and are soluble in alcohol and in alkalis, but do not dissolve in light petroleum. With diazobenzene chloride, it yields *azobenzeneorthomethylcyanacetophenone*, $C_6H_4Me{\cdot}CO{\cdot}CH(CN){\cdot}N_2{\cdot}Ph$, which forms small, yellow, rhombic crystals, melts at 124·7°, and dissolves in boiling alcohol, ether, and alkalis. With sodium hydroxide it yields a derivative which crystallises in yellow silky needles or in yellow plates.

If orthomethylcyanacetophenone is dissolved in cold absolute alcohol saturated with hydrogen chloride, and is allowed to remain for some time, it yields slender needles of the hydrochloride of an ethereal imido-derivative, $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$. When this compound is treated with aqueous ammonia, it yields the free imido-derivative, which crystallises from alcohol in prisms or rectangular tables melting at 116·3°, and soluble in alcohol and ether, but insoluble in alkalis. When boiled with dilute alcohol very slightly acidified with hydrochloric acid, it splits up into ammonium chloride and ethyl orthotoluoylacetate, which separates as an oily liquid when the product is diluted with water. It has an odour similar to that of its lower homologue, ethyl benzoylacetate, and is slightly soluble in alkalis. With ferric chloride, it gives a violet coloration.

The reactions which produce ethyl benzoylacetate and the toluoylacetate constitute a general method for the preparation of the α-ketonic acids. C. H. B.

Preparation of Benzoic Acid. By A. STARTING (*Arch. Pharm.* [3], **27**, 410—411).—The subliming vessel is a copper or brass pan, 3 inches in diameter and 2 inches deep, which is carefully fitted into the bottom of a wooden box, 2¾ feet long by 1 foot wide, and 1 foot deep, either smoothly planed inside or lined with glazed paper. The lid and joints of the box are made tight from the outside. A disc of pasteboard is hung 2 or 3 inches above the pan to prevent the sublimate from falling back into it. The pan is charged with 35 grams of powdered gum benzoïn, and heated for about four hours by means of a small spirit-lamp. The pan is charged a dozen times or more before the box requires emptying. The yield is found to be about 25 per cent. of an acid showing only the faintest trace of yellow colour. J. T.

Pentamethylbenzoic Acid and Durenecarboxylic Acid. By O. JACOBSEN (*Ber.*, **22**, 1215—1224; compare this vol., p. 40).—*Prehnitenedicarboxylic acid*, $C_6Me_4(COOH)_2$ [$(COOH)_2 = 1:2$], is obtained when hexamethylbenzene (20 grams), dissolved in benzene (60 grams), is boiled for two days with nitric acid (2000 grams; 1 vol. acid of sp. gr. 1·4 to 5 vols. water). The acids are extracted from the supernatant benzene by shaking with ammonium carbonate, treated with tin and hydrochloric acid to free them from nitro-compounds, and the prehnitenedicarboxylic acid distilled with steam. It crystallises from hot water in small needles, and from alcohol in compact prisms, melts at 249°, and is readily soluble in alcohol, ether, and benzene, but only very sparingly in cold water. When heated with lime, it yields pure prehnitene. The *barium* salt, $C_6Me_4(COO)_2Ba + 2H_2O$, is readily soluble.

Mellityl chloride, $C_6Me_5\cdot CH_2Cl$, is best prepared by gradually heating hexamethylbenzene (40 grams) with phosphoric chloride (50 grams) at 140°, and repeatedly recrystallising the residue from alcoholic ether, from which it separates in long, rhombic plates. It melts at 99°, boils at about 285° with partial decomposition, and is very readily soluble in ether, benzene, light petroleum, and chloroform, but only sparingly in alcohol.

Mellityl acetate, $C_6Me_5\cdot CH_2\cdot OAc$, prepared by heating a glacial acetic acid solution of the chloride with potassium acetate, crystallises from well-cooled alcohol in small plates or prisms, melts at 85°, boils at about 310°, and is very readily soluble in ether, acetic acid, and warm alcohol, but insoluble in water.

Mellityl alcohol, $C_6Me_5\cdot CH_2\cdot OH$, crystallises from alcohol in large quadratic prisms, melts at 160·5°, and is insoluble in water. When oxidised with chromic acid or dilute nitric acid, it yields polybasic acids, and in the latter case resinous nitro-compounds as well. When treated with potassium permanganate, it is completely destroyed.

Methyl pentamethylphenyl ketone, $C_6Me_5\cdot COMe$, is obtained by adding a solution of pentamethylbenzene (70 grams) in acetic chloride (50 grams) to a well-cooled mixture of aluminium chloride (75 grams) and carbon bisulphide in the course of about an hour, pouring the whole into a large volume of water, and distilling the precipitated ketone with steam. It crystallises from alcohol in nacreous plates, melts at 85°, boils at 285—286°, and is readily soluble in alcohol, ether, chloroform, and glacial acetic acid.

Pentamethylphenylglyoxylic acid, $C_6Me_5\cdot CO\cdot COOH$, is prepared by adding aluminium chloride (15 grams) to a warm solution of pentamethylbenzene (50 grams) in ethyl chloroxalate (40 grams), and warming for about an hour. The product is carefully treated with water, the precipitated ethereal salt washed with warm, dilute hydrochloric acid, hydrolysed by shaking with warm soda, and the alkaline solution separated. The sodium salt, which crystallises from the cold solution, is purified by repeatedly recrystallising, and is then decomposed with hydrochloric acid. Pentamethylphenylglyoxylic acid can also be obtained by oxidising methyl pentamethylphenyl ketone with cold potassium permanganate. It crystallises from warm, dilute alcohol in yellow prisms, melts at 122°, and is readily soluble in alcohol, ether, chloroform, glacial acetic acid, and carbon bisulphide, and moderately easily in hot, but only very sparingly in cold water. When a cold moderately concentrated solution of the sodium salt is treated with hydrochloric acid, the whole solidifies to a colourless mass, but after a few minutes liquefaction ensues, and compact yellow crystals separate from the solution. If the acid is precipitated from a cold dilute solution and kept in the dark, it remains colourless for days, but on exposure to the light it turns yellow; the yellow crystals are also obtained when warm solutions of the sodium salt are acidified.

The *sodium* salt, $C_{13}H_{15}O_3Na + 3H_2O$, crystallises in colourless, nacreous plates, and gradually turns yellow on exposure to light; it is very readily soluble in boiling water, and moderately so in the cold, but only very sparingly in dilute soda. The *barium* salt, $(C_{13}H_{15}O_3)_2Ba + 5H_2O$, forms nodular crystals, and is only very sparingly soluble in cold water. The *copper* salt, $C_{13}H_{15}O_3)_2Cu + 5H_2O$, crystallises in needles, and is readily soluble. The *silver* salt and the *lead* salt are almost insoluble.

Attempts to obtain pentamethylbenzoic acid from the ketone and ketone acid were unsuccessful. Potassium permanganate or chromic acid first converts the ketone into the acid, and then oxidises it completely.

Mercury dipentamethylphenyl, $Hg(C_6Me_5)_2$, was obtained by treating bromopentamethylbenzene with sodium amalgam. It is almost insoluble in alcohol, and only very sparingly soluble in ether, but it dissolves freely in hot xylene, from which it crystallises in small prisms melting at 266°; it distils at a higher temperature with partial decomposition.

Pentamethylbenzoic acid, $C_6Me_5{\cdot}COOH$, can be easily prepared by mixing pentamethylbenzene (70 grams) with carbonyl chloride (50 grams), cooled to −10°, gradually adding aluminium chloride (5—10 grams), and keeping the mixture at a temperature below 0° for two weeks. The whole is then exposed to moist air for some time, treated with water, warmed with soda, the alkaline solution separated and acidified with hydrochloric acid. It is almost insoluble in cold water, and crystallises from boiling water in slender needles; it separates from hot 70 per cent. alcohol, in which it is readily soluble, in long, thin prisms, melts at 210·5°, is volatile with steam, and distils without decomposition when heated carefully. When heated at 200° with fuming hydrochloric acid, or when distilled over lime, it is converted into pentamethylbenzene. The *calcium* salt, $(C_{12}H_{15}O_2)_2Ca$, is rather sparingly soluble in cold water, and crystallises in small, compact, well-defined prisms. The *barium* salt, $(+2H_2O)$, is much more readily soluble in warm water, and crystallises on cooling in long, thin plates. The *methyl* salt, $C_{12}H_{15}O_2Me$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from ethyl and methyl alcohol, in which it is readily soluble, in large plates, melts at 67·5°, and boils at 299—300° (thermometer entirely in vapour). It is not acted on by boiling concentrated alcoholic potash, but when heated therewith at 200—220° it is quickly hydrolysed.

The *amide*, $C_6Me_5{\cdot}CO{\cdot}NH_2$, prepared by treating pentamethylbenzene with carbamide chloride and aluminium chloride in carbon bisulphide solution, crystallises from alcohol in rhombic plates, melts at 206°, and is almost insoluble in cold, and only sparingly soluble in hot water. It is very slowly acted on by strong boiling alcoholic potash, but it is converted into pentamethylbenzene when heated at above 150° with concentrated hydrochloric acid. The nitrile, $C_6Me_5{\cdot}CN$, can be easily obtained by heating the acid with lead thiocyanate. It crystallises from alcohol in long needles, melts at 170°, boils at 294—295° (compare Hofmann, Abstr., 1885, 1129), and is insoluble in water. It is not acted on by alcoholic potash even at 220°, but when heated at 220—230° with concentrated hydrochloric acid, it is quickly decomposed into ammonia, pentamethylbenzene, and carbonic anhydride.

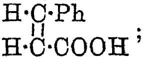
Pentamethylbenzoic acid dissolves in cold sulphuric acid, forming a colourless solution; on keeping for some time at the ordinary temperature, carbonic anhydride and sulphurous anhydride are evolved, and the solution gradually becomes reddish-yellow, but even after 8 to 14 days a large quantity of acid is unchanged. If the solution is poured into water and the precipitate treated with sodium carbonate, there remains a brown substance, consisting of hexamethylbenzene and coloured compounds of higher melting point. The former can, with difficulty, be obtained in a pure state by distilling under diminished pressure and recrystallising from a mixture of toluene and alcohol. The sulphuric acid solution contains prehnitenesulphonic acid. Pentamethylbenzoic acid is also decomposed by a cold mixture of nitric acid and sulphuric acid; carbonic anhydride is rapidly evolved, and dinitroprehnitene (m. p. 178°) and the resinous decomposition products of hexamethylbenzene are formed.

Durenecarboxylic acid, $C_6HMe_4{\cdot}COOH$, can be prepared by treating durene with aluminium chloride and carbonyl chloride, and decomposing the resulting chloride as described above. It crystallises from dilute alcohol in large plates, melts at 179°, and is very sparingly soluble in cold, but rather more readily in hot water. It is volatile with steam, and when carefully heated can be distilled without decomposition. When heated at 200—220° with concentrated hydrochloric acid it is decomposed into durene and carbonic anhydride. The acid (m. p. 180°) obtained by Meyer and Ador (*Jahresb.*, 1879, 562) by oxidising durylbenzoyl with potassium permanganate, is probably identical with the acid described above, but the durenecarboxylic acid (m. p. 109°) obtained by Claus and Foecking (Abstr., 1888, 276) cannot be identical with this compound. The *calcium* salt, $(C_{11}H_{13}O_2)_2Ca$, crystallises in short, compact prisms, and is sparingly soluble in both hot and cold water. The *barium* salt, $(+4H_2O)$, is moderately soluble in hot water, from which it crystallises in small plates. The *methyl* salt, $C_{11}H_{13}O_2Me$, crystallises from alcohol in plates, melts at 59°, and boils at 268—269°. It is hardly acted on at all by boiling alcoholic potash, but when heated therewith at 210° it is quickly hydrolysed. The *nitrile*, $C_6HMe_4{\cdot}CN$, prepared by distilling the acid with lead thiocyanate, crystallises from alcohol, in which it is very readily soluble, in long needles melting at 76—77°. It is not acted on by concentrated hydrochloric acid at temperatures below 210°, but at 220—230° it is decomposed into durene and carbonic anhydride.

Durenecarboxylic acid dissolves unchanged in cold sulphuric acid, but the solution gradually becomes brown, and carbonic anhydride and sulphurous anhydride are evolved, although, even after several weeks, the acid is only partially decomposed. The reaction is seemingly similar to that which occurs in the case of pentamethylbenzoic acid, as at least two sulphonic acids and a brown substance, probably decomposition products of hexamethylbenzene, are formed.

F. S. K.

Conversion of Acetylene into Ethylene-derivatives by the direct Addition of Hydrogen. By L. ARONSTEIN and A. F. HOLLEMAN (*Ber.*, **22**, 1181—1184; compare this vol., p. 51).—When phenylpropiolic acid is boiled for a few hours with zinc-dust and glacial acetic acid, it is converted into cinnamic acid. Assuming that no intramolecular change takes place, this reaction seems to show that cinnamic acid, in accordance with Wislicenus' views, has the configuration

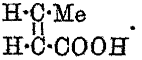


$$\begin{array}{c}\mathrm{H{\cdot}C{\cdot}Ph}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$$

; on the other hand, the formation of phenyl cinnamate by heating diphenyl fumarate (Anschütz) rather points to an axially symmetrical configuration.

Ethyl dibromohydrocinnamate melts at 74—75°; Anschütz and Kinnicut (Abstr., 1878, 981) give 69° as the melting point of this compound.

Tetrolic acid is reduced to butyric acid when boiled with sodium and methyl alcohol, but when treated with 3 per cent. sodium amalgam, it is converted into solid crotonic acid (m. p. 72°), and no butyric acid or isocrotonic acid is formed. Assuming that no intramolecular change takes place, the conversion of tetrolic acid into solid crotonic acid is a proof that the latter has the configuration



$$\begin{array}{c}\mathrm{H{\cdot}C{\cdot}Me}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}.$$

Acetylenedicarboxylic acid is reduced when warmed at 50—60° for two days with zinc-dust and glacial acetic acid, and is converted into succinic acid, but no maleic acid or fumaric acid is formed.

When phenylacetylene is boiled for several hours with glacial acetic acid and zinc-dust, it is converted into cinnamene.

F. S. K.

Ethyl Dihydroxyquinonedicarboxylate and its Hydro-derivatives. By M. BÖNIGER (*Ber.*, **22**, 1284—1294).—Ethyl dihydroxyquinonedihydrodicarboxylate was dissolved in dilute soda, the solution kept for 24 hours, filtered and carefully mixed in the cold with concentrated sulphuric acid. After repeatedly recrystallising the product, it melted at 151°, and showed all the properties of the unsymmetrical tetrahydroxybenzene described by Löwy (Abstr., 1886, 1028). The pure, finely divided substance was suspended in water, and treated with chlorine; it was converted into a compound (m. p. 93°) identical with the ethereal salt first prepared by Löwy (*loc. cit.*) by treating ethyl dihydroxyquinonedicarboxylate with chlorine, and which was subsequently proved by Zeckendorf (Abstr., 1887, 727) to be ethyl tetrachlorodiketoadipate, $C_{10}H_{10}Cl_4O_6$. By these and other experiments, it was proved that Löwy's tetrahydroxybenzene is in reality ethyl dihydroxyquinonedicarboxylate.

Ethyl dihydroxyquinonedicarboxylate forms a *diacetyl*-derivative, $C_6O_2(OAc)_2(COOEt)_2$ which crystallises from glacial acetic acid in yellowish needles, melting at about 174° with decomposition; it is insoluble in cold water, but when heated under water it turns red, and is decomposed into acetic acid and ethyl dihydroxyquinonedicarboxylate.

When ethyl dihydroxyquinonehydrodicarboxylate is exposed to the air in alkaline solution, oxidation ensues, and ethyl dihydroxyquinonecarboxylate is formed; in absence of air, the hydro-ethereal salt is not hydrolysed at the ordinary temperature, but on heating, the solution gradually darkens, and the basic sodium salt of dihydroxyquinonedicarboxylate, described by Löwy, separates.

The basic sodium salt of tetrahydroxyterephthalic acid described by Löwy is in reality a salt of dihydroxyquinonedicarboxylate, and the neutral sodium salt of tetrahydroxyterephthalic acid is a mixture of the sodium-derivatives of ethyl dihydroxyquinonedihydrodicarboxylate and ethyl dihydroxyquinonedicarboxylate.

The parahydroxyquinone prepared by Löwy by hydrolysing ethyl dihydroxyquinonedicarboxylate, is identical with that obtained from diamidoresorcinol by Nietzki and Schmidt.

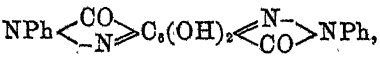
Ethyl dihydroxyquinonedicarboxylate and ethyl dihydroxyquinonehydrodicarboxylate both yield the same product with hydroxylamine; this substance has the composition $C_6O_2(ONH_3{\cdot}OH)_2(COOEt)_2$, and was proved to be a hydroxyammonium salt of ethyl dihydroxyquinonedicarboxylate.

The compound $(COOEt)_2C_6O_2(OH)_2,(N_2H_3Ph)_2$ separates in the form of a golden, microcrystalline powder when a cold alcoholic solution of ethyl dihydroxyquinonedicarboxylate is shaken with excess of phenylhydrazine. It crystallises from boiling alcohol in small needles, melts at 134°, and is insoluble in water, and only sparingly soluble in cold alcohol and ether. It is decomposed into phenylhydrazine and the original ethereal salt by dilute sodium carbonate solution.

Ethyl dihydroxyhydroquinonedicarboxylate does not react with phenylhydrazine in the cold, but when boiled therewith for about an hour in alcoholic solution, the salt (m. p. 134°) just described separates from the solution on cooling.

The compound $C_{20}H_{12}N_4O_4,NHPh{\cdot}NH_2$ is formed when ethyl dihydroxyquinonedicarboxylate or ethyl dihydroxyquinonehydrodicarboxylate is boiled for about six hours with an alcoholic solution of phenylhydrazine. The cold solution is filtered from a sparingly soluble bye-product which is also formed in the reaction, diluted with a large volume of water, acidified with acetic acid, and the flocculent precipitate purified by redissolving in alcohol and reprecipitating with water and acetic acid. It is a carmine-red powder which decomposes at 130—140°, and is insoluble in water, but readily soluble in alcohol, ether and benzene with an intense red coloration. It dissolves in concentrated sulphuric acid with a bluish-red coloration, and it is decomposed by mineral acids into dihydroxybenzodiphenyldipyrazolone, $C_{20}H_{12}N_4O_4$, and phenylhydrazine.

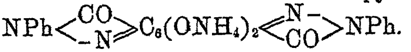
Dihydroxybenzodiphenyldipyrazolone,



$$\mathrm{NPh}<\begin{matrix}\mathrm{CO}\\ \mathrm{-N}\end{matrix}>\mathrm{C_6(OH)_2}<\begin{matrix}\mathrm{N-}\\ \mathrm{CO}\end{matrix}>\mathrm{NPh},$$

separates in the form of a reddish-brown powder when an alcoholic solution of the preceding compound is boiled with hydrochloric acid and then diluted with water. It begins to decompose at about 125°, melts at about 150°, and is rather more sparingly soluble in ether and alcohol than the phenylhydrazine salt described above.

The sparingly soluble bye-product referred to above is the diammonium-derivative of the dipyrazolone, and has the constitution



$NPh<\overset{CO}{\underset{-N}{}}>C_6(ONH_4)_2<\overset{N-}{\underset{CO}{}}>NPh$. It is an ochre-coloured powder, decomposes at about 220°, and is moderately easily soluble in water and boiling alcohol. When warmed with alkalis, it is decomposed with evolution of ammonia, and when treated with acids it is converted into the dipyrazolone. F. S. K.

Constitution of Ethyl Bromodinitrophenylmalonate. By C. L. JACKSON (*Ber.*, **22**, 1232—1233; compare Abstr., 1888, 1091).—Ethyl bromodinitrophenylmalonate can be readily and quantitatively converted into bromodinitrophenylacetic acid, melting at 177°, and from the latter Grete's bromodinitrotoluene (m.p. 103—104°) is easily obtained. When this bromodinitrotoluene is heated with alcoholic ammonia, it yields a dinitrotoluidine (m. p. 193°) identical with that prepared by Hepp by treating γ-trinitrotoluene with alcoholic ammonia. As this dinitrotoluidine yields a dinitrotoluene melting at 71°, which has the constitution [$Me : (NO_2)_2 = 1 : 2 : 4$], it has itself the constitution [$Me : NH_2 : (NO_2)_2 = 1 : 3 : 4 : 6$], and is identical with the dinitrotoluidine described by Staedel (this vol., p. 497). Ethyl bromodinitrophenylmalonate has therefore the constitution [$CH(COOEt)_2 : Br : (NO_2)_2 = 1 : 3 : 4 : 6$.]

When ethyl dinitrophenylmalonate is treated with aniline, it yields ethyl anilidodinitrophenylmalonate. F. S. K.

Carvole and Carvacrolsulphonic Acid. By A. CLAUS and W. FAHRION (*J. pr. Chem.* [2], **39**, 356—366).—*Carvacrolparasulphonic acid*, $C_{10}H_{14}SO_4$, is obtained by the action of strong sulphuric acid on carvole and also on carvacrol; it crystallises (with 2 mols. H_2O) in large tables or flattened monoclinic prisms soluble in water and alcohol, and melting at 65—69° (uncorr.); when further heated it decomposes, evolving a smell of carvacrol. The *potassium* and *sodium* salts (each with 1 mol. H_2O), the *calcium*, *barium*, and *lead* salts (each with 5 mols. H_2O) are described, as are also the *chloride* and *amide*. When oxidised carvacrolparasulphonic acid is converted into thymoquinone.

Acetic anhydride in presence of sodium acetate does not yield an acetyl-derivative with carvole. *Acetylcarvacrol* is a thick, pale-yellow oil of not unpleasant odour, boiling at 244—245° (uncorr.).

The paper concludes with some remarks as to the constitution of carvole, which shows the properties of a ketone. A. G. B.

Orthonitrosulphanilic Acid. By J. Z. LERCH (*Chem. Centr.*, 1889, 286, from *Listy Chem.*, **13**, 85—89).—*Orthonitrosulphanilic acid*, $NH_2{\cdot}C_6H_3(NO_2){\cdot}SO_3H$ (1 : 2 : 4), is prepared from acetanilide by the action of fuming sulphuric acid and nitration of the cooled mixture. The sulpho-group is readily eliminated, heating with water or dilute sulphuric or hydrochloric acid being sufficient to cause this to take place. By heating with potash the amido-group is eliminated with formation of the salt $KO·C_6H_3(NO_2)·SO_3H$.

Orthophenylenediamineparasulphonic acid,

$$C_6H_3(NH_2)_2·SO_3H\ [= 1 : 2 : 4],$$

is obtained from the above-named acid by reduction with stannous chloride. It is sparingly soluble in cold water, more readily in hot, nearly insoluble in cold alcohol, and little more so in hot. It crystallises in needles which become blue when warmed. Nietzki's reaction with croconic acid produced a black precipitate of the azine.

Orthonitroazobenzeneparasulphonic acid, prepared from the last named acid by the action of sodium nitrite and hydrochloric acid in the cold, forms long, yellow pyramids, nearly insoluble in water and insoluble in cold alcohol; these explode when heated.

Orthonitrohydrazinebenzeneparasulphonic acid,

$$NO_2·C_6H_3(NH·NH_2)·SO_3H,$$

is prepared from the azo-acid by reduction with stannous chloride. It forms yellow needles, somewhat soluble in warm water, nearly insoluble in alcohol, readily soluble in alkaline solutions.

Sodium nitrotartrazinesulphonate,

$$C_2(COOH)_2[N·NH·C_6H_3(NO_2)·SO_3Na]_2,$$

prepared from orthonitrophenylbenzeneparasulphonic acid by the action of sodium dihydroxytartrate, forms a crystalline, yellowish-red powder, readily soluble in water and alkaline solutions. The solution in concentrated potash is dark-green, which becomes red when diluted.

Orthoamidohydrazinebenzeneparasulphonic acid,

$$NH_2·C_6H_3(NH·NH_2)·SO_3H,$$

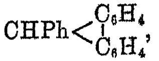
prepared from the nitro-diazo-acid by reduction, first with stannous chloride and then with zinc and hydrochloric acid, forms small, colourless needles which decompose at 100°. They are nearly insoluble in cold and sparingly soluble in hot alcohol; readily soluble in alkaline solutions. Croconic acid renders the solution dark coloured, and precipitates crystals of the azine. J. W. L.

Orthosulphobenzoic Acid and its Derivatives. By I. REMSEN (*Ber.*, **22**, 1185).—A reply to Fahlberg and Barge (this vol., p. 709). The author and Linn (*ibid.*, 710) have ascertained the true character of orthosulphobenzoic acid, and of the reaction between resorcinol and ammonium hydrogen orthosulphobenzoate. They have also shown that when dihydroxybenzoylbenzenesulphonic acid is heated at 185° for a few hours, it is converted into the true sulphonefluoresceïn. The anhydride of orthosulphobenzoic acid has been obtained in a pure state by heating the acid with phosphoric anhydride. When benzoic sulphinide is boiled with dilute acids, it is readily converted into ammonium hydrogen orthosulphobenzoate. These facts render the analysis of commercial "saccharin" an easy matter, and it has been found that the commercial article contains

40—45° per cent. of sulphinide, but that more than half consists of parasulphaminebenzoic acid. F. S. K.

Action of Potassium on Triphenylmethane. By M. HANRIOT and O. SAINT-PIERRE (*Compt. rend.*, **108**, 1119—1121).—These experiments were made with a view to ascertain whether the phenyl-groups, which are known to reduce the activity of the basic function of the phenylamines, confer an acid function on the methane hydrogen in triphenylmethane.

Sodium has no action even on boiling triphenylmethane, but if the latter is heated with potassium at 200° in an inert atmosphere, the metal gradually disappears with evolution of hydrogen and formation of a red substance which is very unstable and could not be isolated.

Above 250° more hydrogen is evolved, and the product is much darker and contains the potassium-derivative of a hydrocarbon containing less hydrogen than triphenylmethane. If this product is treated with hydrochloric acid it yields the hydrocarbon $C_{19}H_{14}$, which melts at 148·5°, boils above 360°, and is purified by dissolving it in chloroform, and precipitating by addition of light petroleum. It seems to be identical with Hemilian's hydrocarbon,  $CHPh<\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, but the orthobenzoylbenzoic acid which it yields on oxidation, is derived from impurities in the triphenylmethane, and the true product is benzophenone. It does not yield triphenyl carbinol, diphenic acid, nor diphenylene ketone, and hence would seem more probably to have the constitution $C_6H_4{:}CPh_2$. When treated with bromine in the cold in presence of chloroform, it yields a dibromide, $C_{19}H_{14}Br_2$, which melts at 187°. Under other conditions it yields a monobromo-derivative, $C_{19}H_{13}Br$, which crystallises from alcohol and melts at 110°. When dissolved in fuming nitric acid, it yields small crystals of the dinitro-derivative $C_{19}H_{12}(NO_2)_2$, which are almost insoluble in benzene, ethyl alcohol, and chloroform, and melt with decomposition at about 240°.

The potassium-derivative of triphenylmethane absorbs carbonic anhydride at 200° and becomes white. When this product is dissolved in water, precipitated by hydrochloric acid, and crystallised from ether, it melts at 264°, with loss of carbonic anhydride, and yields triphenylmethane melting at 94°. It follows that the product is triphenylacetic acid.

The prolonged action of chlorbenzene on the potassium-derivative in presence of benzene yields the compound $C_{25}H_{22}$, which crystallises from light petroleum and melts at 140°. It yields a mono bromo-derivative melting at 177°.

Benzoic chloride yields the compound $C_{26}H_{18}O$, which separates from boiling benzene in small crystals melting at 172°. This compound can be purified by crystallisation from acetone. Alcoholic potash converts it into the hydrocarbon $C_{19}H_{14}$ and benzoic acid, and hence it would seem to be *benzoylphenylenediphenylmethane*. Hydriodic acid and phosphorus convert it into the hydrocarbon $C_{26}H_{20}$, which melts at 234° after crystallisation from a mixture of benzene and alcohol. C. H. B.

Tetraphenylsuccinonitrile. By K. AUWERS and V. MEYER (*Ber.*, **22**, 1227—1229).—*Tetraphenylsuccinonitrile*, $CN\cdot CPh_2\cdot CPh_2\cdot CN$, is formed when diphenylacetonitrile (2 mols.), prepared by Neure's method (this vol., p. 597), is added to an absolute alcoholic solution of sodium (1 mol.), and the resulting sodium compound treated gradually with an ethereal solution of iodine (1 mol.). The whole is mixed with water, and the undissolved nitrile purified by washing with water and hot alcohol. The yield is quantitative. It crystallises from hot, glacial acetic acid in small, flat needles, and is very sparingly soluble in hot alcohol, ether, and light petroleum, but readily in chloroform and carbon bisulphide. It melts at about 230° when heated very quickly, but it has no well-defined melting point, as it is gradually decomposed at a much lower temperature, and can be liquefied by heating for a long time at 180°. This compound is identical with the substance obtained by Neure (*loc. cit.*), by treating diphenylacetonitrile with nitrous acid, and also with the isodiphenylacetonitrile obtained by Anschütz and Romig (Abstr., 1886, 1033) as a bye-product in the reduction of diphenylethanedinitrile.

F. S. K.

Isomeric Methyldeoxybenzoïns. By H. STRASSMANN (*Ber.*, **22**, 1229—1231).—Paratolylacetic acid is best prepared by hydrolysing the nitrile with hydrochloric acid. The acid thus obtained is identical with that prepared by Radziszewski (Abstr., 1885, 889), and melts at 94°, but in one experiment an acid, melting at 192° was formed, the silver salt of which contained 41·77 per cent. of silver. *Sodium paratolylacetate*, $C_9H_9O_2Na$, crystallises in colourless needles, and is moderately soluble in water.

Paraxylyl phenyl ketone, $C_6H_4Me\cdot CH_2\cdot COPh$, prepared by treating paratolylacetic chloride with benzene in presence of aluminium chloride, crystallises in colourless, quadratic prisms melting at 94°. It does not combine with hydroxylamine when heated therewith in alcoholic solution, but the *oxime*, a colourless, crystalline compound, melting at 109°, can be readily obtained from the ketone by Auwers' method (this vol., p. 689).

The isomeric paratolyl benzyl ketone, $C_6H_4Me\cdot CO\cdot CH_2Ph$, prepared by Mann (Abstr., 1881, 1034), crystallises in colourless plates melting at 109°. The *oxime* $C_{15}H_{15}NO$, prepared by boiling an alcoholic solution of the ketone with hydroxylamine, crystallises in colourless plates and melts at 131°. F. S. K.

Action of Ammonium Formate on Deoxybenzoïn. By R. LEUCKART and H. JANSSEN (*Ber.*, **22**, 1409—1413).—*Symmetrical diphenylethylamine*, $CH_2Ph\cdot CHPh\cdot NH_2$, is obtained by heating one part of deoxybenzoïn and two parts of ammonium formate at 220—230° for 4—5 hours. The solid product is saponified by boiling with alcoholic potash in a reflux apparatus for 2—3 hours, and the amine separated by distillation with steam, and purified by conversion into its hydrochloride, which is subsequently decomposed with aqueous soda. It boils without decomposition at 309—310° under a pressure of 737 mm., is soluble in water and alcohol, sparingly soluble in ether, yielding solutions having a strongly alkaline reaction, and on exposure to the air is rapidly converted into the carbamate and to some extent into the carbonate.

The *hydrochloride*, $C_{14}H_{15}N,HCl$, crystallises in colourless, long needles; the *platinochloride*, $(C_{14}H_{15}N)_2,H_2PtCl_6$, forms yellow scales; the *mercurochloride* crystallises in long scales, and the *nitrate* and *sulphate* also crystallise well. When boiled with a solution of an equimolecular proportion of sodium nitrite, the hydrochloride is converted into toluylene hydrate. The *carbamide* crystallises in small needles and melts at 98—99°; the *phenylcarbamide* crystallises in needles and melts at 129°; the *phenylthiocarbamide* crystallises in small scales and melts at 170°; the *acetyl*-derivative crystallises in long needles and melts at 148°; the *benzoyl*-derivative forms small needles and melts at 177—178°. W. P. W.

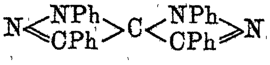
Bromo-derivatives of Dibenzyl Ketone. By E. BOURCART (*Ber.*, **22**, 1368—1370).—When dibenzyl ketone is treated with the vapour of bromine in carbon bisulphide solution, the following four compounds are formed according to the quantity of bromine employed. They all lose the whole of their bromine when boiled with water or alcohol.

Bromodibenzyl ketone, $CHPhBr\cdot CO\cdot CH_2Ph$, crystallises in needles, melts at 43—44°, and is readily soluble in alcohol.

Dibromodibenzyl ketone crystallises from light petroleum in needles and melts at 110—111°. When heated with magnesia in alcoholic solution, it yields two compounds having the composition $C_{15}H_{10}O_2$ and $C_{15}H_{10}O$ respectively.

Tribromodibenzyl ketone, $CHPhBr\cdot CO\cdot CBr_2Ph$, is more easily formed than any of the other compounds, from which it can be separated by means of light petroleum. It melts at 81° and is readily soluble in warm, but only sparingly in cold, light petroleum. When heated with water it yields three compounds, two of which have the composition $C_{15}H_{10}O$ and $C_{30}H_{22}O_5$ respectively. Tribromodibenzyl ketone (2 mols.) combines with phenylhydrazine (3 mols.); the product melts at 55—60° and resembles the corresponding derivative of tetrabromodibenzyl ketone, but, unlike the latter, it contains oxygen.

Tetrabromodibenzyl ketone, $CBr_2Ph\cdot CO\cdot CBr_2Ph$, melts at 84—85°, and is more readily soluble in light petroleum than the tribromoketone; when heated with water or alcohol, it yields several compounds, none of which contains bromine. The compound



$$\mathrm{N}\ll\begin{matrix}\mathrm{NPh}\\\mathrm{CPh}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{NPh}\\\mathrm{CPh}\end{matrix}\gg\mathrm{N}$$

is obtained when the tetrabromo-ketone is heated at 150° with an alcoholic solution of phenylhydrazine. It is readily soluble in alcohol, ether, and chloroform, but only sparingly in light petroleum and insoluble in water and dilute acids; on adding water to the alcoholic solution it is precipitated as a brownish-yellow powder melting at 65—70°. When treated with nitric acid, it is converted into a bright-yellow compound, soluble in glacial acetic acid.

F. S. K.

Benzilic Acid and its Derivatives. By H. KLINGER and O. STANDKE (*Ber.*, **22**, 1211—1215).—*Acetylbenzilic acid*,

$$OAc\cdot CPh_2\cdot COOH,$$

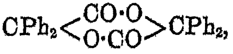
prepared by treating benzilic acid with acetic anhydride, crystallises from glacial acetic acid in slender or compact needles, melts at 98°, and is reconverted into the acid when heated at 100—110°, or when warmed with aqueous alkalis.

Methyl benzilate, $OH\cdot CPh_2\cdot COOMe$, is obtained by treating the potassium salt with methyl iodide; it crystallises well and melts at 74—75°. The *ethyl* salt, prepared in like manner, crystallises in brittle prisms or needles melting at 34°. The *benzyl* salt is crystalline, and melts at 75—76°. Boiling aniline seems to have no action on these ethereal salts.

When hydrogen chloride is passed into an alcoholic solution of benzilic acid, impure ethyl diphenylchloracetate is obtained, and not ethyl benzilate as stated by Jena.

Ethyl diphenylanilidoacetate, $NHPh\cdot CPh_2\cdot COOEt$, prepared by treating ethyl diphenylchloracetate with aniline, melts at 114—115°, and is not acted on by boiling aniline. The free *acid* crystallises in needles, melts at 168° with decomposition and previous softening, is very sparingly soluble in water, and is decomposed when recrystallised from alcohol or benzene. It dissolves in cold, concentrated sulphuric acid with a yellow coloration which, on warming suddenly changes to carmine-red. The *silver* salt is very unstable. The *methyl* salt melts at 106—107°.

When benzilic acid is heated for a long time at 180° it is chiefly decomposed into water, carbonic oxide, and benzophenone, but a small portion is converted into a dark-red, resinous substance from which no crystalline compound could be isolated. The formation of dibenzilic acid and ethyldibenzoïn which, according to Jena, takes place under these conditions, was not observed in any experiments.

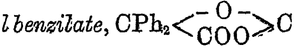
Benzilide,  $CPh_2{<}\substack{CO\cdot O\\ O\cdot CO}{>}CPh_2$, is formed together with carbonic oxide and dibenzilic acid when benzilic acid is treated with phosphorus pentoxide. It crystallises from alcohol in long, colourless needles melting at 196°, and from benzene with 1 mol. of benzene in quadratic prisms which quickly effloresce. It is not acted on by acetic chloride, but it is readily converted into benzilic acid by alcoholic potash. It dissolves in concentrated sulphuric acid with a red coloration which disappears on adding water.

Cahours states that when benzilic acid is treated with phosphoric chloride, benzilic chloride, $OH\cdot CPh_2\cdot COCl$, boiling at 270°, is obtained. The authors' experiments seem to show that this liquid is a mixture of benzophenone and benzophenone chloride as, although benzilic chloride and diphenylchloracetic chloride are both formed in the above reaction, they are decomposed when distilled.

Benzilic amide, $OH\cdot CPh_2\cdot CONH_2$, prepared by treating the chlorides obtained as described above with ammonium carbonate, crystallises from dilute ammonia in small plates, and from chloroform in plates or prisms; it melts at 154—155°, and is slowly decomposed when warmed with potash.

When benzilic acid (2 mols.) is dissolved in concentrated sulphuric acid, carbonic oxide (1 mol.) is evolved, and various compounds are formed according to the temperature employed. At the ordinary temperature the chief products are compounds insoluble in water, amongst which benzhydrol benzilate is the most important.

Benzhydrol benzilate,



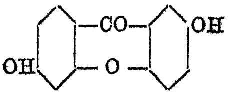
$CPh_2<\begin{matrix}-O-\\ COO\end{matrix}>CPh_2$

a colourless, amorphous, very electrical powder, melts at about 100°, and gives the benzilic acid reaction with concentrated sulphuric acid. It is very stable towards alkalis, oxidising agents, and phosphoric chloride, but when heated with copper oxide it yields benzophenone, and, with soda-lime, tetraphenylethane.

A crystalline compound, $C_{21}H_{13}O_2$, is also formed in very small quantities by the action of sulphuric acid on benzilic acid at the ordinary temperature. It melts at 256—257°, and, when treated with alcoholic potash, it is converted into an acid melting at 232°.

When benzilic acid is dissolved in concentrated sulphuric acid at 100° the principal products are two sulphonic acids which have the composition $C_{26}H_{20}SO_5$ and $C_{27}H_{20}SO_6$ respectively. These acids dissolve in water, forming colourless solutions which, on evaporating, yield carmine-red residues—the colour disappearing again on moistening slightly. The sodium salts crystallise well. F. S. K.

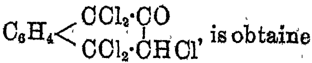
Synthesis of Euxanthone. By C. GRAEBE (*Ber.*, 22, 1405—1406).—The author states that he has effected the synthesis of euxanthone by treating a mixture of β-resorcylic acid and quinolcarboxylic acid with acetic anhydride and distilling the resulting product. The formula of euxanthone must, therefore, be



Details are reserved for a later communication. W. P. W.

Action of Chlorine on β-Naphthol. By T. ZINCKE (*Ber.*, 22, 1024—1035).—The compound (pentachloroketohydronaphthalene) obtained by treating α-trichloroketohydronaphthalene with chlorine in acetic acid solution (compare this vol., p. 265), has been proved to be a compound of tetrachloro-β-ketonaphthalene with hexachloro-β-ketonaphthalene (see below).

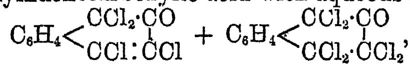
α-Pentachloro-β-ketohydronaphthalene,



$C_6H_4<\begin{matrix}CCl_2\cdot CO\\ |\\ CCl_2\cdot CHCl\end{matrix}$

is obtained when a stream of dry chlorine is passed for a long time through a solution of α-trichloroketohydronaphthalene in carbon bisulphide (15—20 parts), moist air being carefully excluded; after keeping for

12 hours the solution is quickly evaporated, the residue washed with a little light petroleum, and crystallised from carbon bisulphide. It separates in large, transparent crystals, melts at 123°, turns yellow on exposure to the light, and, when kept for a long time, the crystals become opaque. It is only sparingly soluble in light petroleum, but moderately so in benzene and readily in ether, with partial decomposition; it is also quickly decomposed into hydrogen chloride and tetrachloro-β-ketonaphthalene by alcohol and glacial acetic acid. It is very readily converted into trichloro-β-naphthol by reducing agents, so that in most respects it behaves like the last-named compound; it yields anilidochlorhydroxynaphthaquinone (m. p. 253°) with aniline, an ethoxy-derivative (compare Abstr., 1888, 708) with alcoholic potash, and dichlorohydroxyindenecarboxylic acid with aqueous alkalis.

The compound,  $C_6H_4<\begin{matrix}CCl_2\cdot CO\\ |\quad\ \ |\\ CCl:CCl\end{matrix} + C_6H_4<\begin{matrix}CCl_2\cdot CO\\ |\quad\ \ |\\ CCl_2\cdot CCl_2\end{matrix}$, which was previously described as pentachloroketohydronaphthalene, can be obtained by treating α-α-dichloro-β-naphthol or α-trichloro-β-ketohydronaphthalene with excess of chlorine, but it is most conveniently prepared by dissolving its constituents (equal molecules) in ether, adding light petroleum, and allowing the solution to evaporate slowly. It crystallises from glacial acetic acid in large, well-defined, rhombic double pyramids, similar in form and colour to crystals of sulphur. It separates from a mixture of ether and light petroleum in large, shining crystals, and melts at 86—87° to a turbid liquid which only becomes clear at 96°. The molecular weight, determined by Raoult's method in glacial acetic acid solution, was found to be 314·5 as a mean of two experiments. F. S. K.

Nitroso- and Dinitroso-naphtharesorcinol. By S. v. KOSTANECKI (*Ber.*, 22, 1342—1347).—*Hydroxynaphthaquinoneoxime* (*nitrosonaphtharesorcinol*), [NOH : OH : O = 1 : 2 : 4], prepared by treating hydroxynaphthaquinone with hydroxylamine hydrochloride or potassium hydroxylaminesulphonate, crystallises from dilute acetic acid in yellow needles, and decomposes at 180°. It is readily soluble in hot alcohol, alkalis, and sodium carbonate, but only very sparingly in hot water and insoluble in ether. It gives a brownish-yellow coloration with concentrated sulphuric acid, and in alcoholic solutions ferrous salts produce a green, ferric salts a dark brown, copper sulphate a dark yellow, and nickel salts a scarlet precipitate. It forms olive-green compounds with iron mordants.

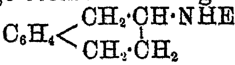
Chloronitrosonaphtharesorcinol, [NOH : OH : Cl : O = 1 : 2 : 3 : 4], prepared from chlorhydroxynaphthaquinone in like manner, crystallises from acetic acid in yellow needles, and decomposes at 178°. The reactions with metallic salts are similar to those given by the preceding compound, and, like the latter, it forms coloured compounds with mordants.

Dinitrosoresorcinol crystallises with 1 and not with 2 mols. H_2O as stated by Fitz (*Ber.*, 8, 631); it can be obtained by treating nitrosoresorcinol with nitrous acid.

Dinitrosonaphtharesorcinol, [$(NOH)_2 : O_2$ = 1 : 3 : 2 : 4], can be

obtained by pouring a dilute alkaline solution of nitrosonaphtharesorcinol and sodium nitrate into dilute hydrochloric acid. It crystallises from alcohol in yellowish plates, decomposes at 165°, and is converted into phthalic acid by dilute nitric acid. It dyes mordanted materials the same colours as dinitrosoresorcinol, but the shades are darker. When reduced with zinc and hydrochloric acid, it yields an amidohydroxynaphthaquinone, [$O_2 : OH : NH_2 = 1 : 4 : 2 : 3$], identical with the compound described by Merz and Weith (*Ber.*, **11**, 1319).
F. S. K.

Reduction of Alkyl β-Naphthylamines. By E. Bamberger and R. Müller (*Ber.*, **22**, 1295—1311; compare Bamberger, this vol., p. 717, and Bamberger and Filehne, *ibid.*, 737).—Pure ethyl-β-naphthylamine is a colourless, mobile liquid boiling at 305° (716 mm.; 191°; 25 mm.); it quickly turns brown on exposure to the air, and gives a ponceau-red dye with diazosulphanilic acid. Solutions of the salts are not changed by ferric chloride in the cold, but on boiling they turn pale-green, then dirty-brown, and finally greenish-brown; potassium dichromate and sulphuric acid produce a brown coloration, the solution becomes turbid, and a yellowish-brown, flocculent precipitate forms, but no further change occurs on heating.



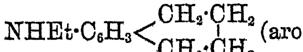
Ethyl-β-tetrahydronaphthylamine, $C_6H_4<\begin{matrix}CH_2\cdot CH\cdot NHEt\\ | \\ CH_2\cdot CH_2\end{matrix}$ (alicylic), is obtained, together with the isomeric aromatic base (see below), when ethyl-β-naphthylamine (15 grams) is reduced with sodium (24 grams) and amyl alcohol as previously described (*loc. cit.*). The aqueous and amyl alcoholic solutions are distilled separately with steam, the bases collected in hydrochloric acid, the solutions mixed together, and treated with animal charcoal. The free bases are then dissolved in light petroleum, and a stream of moist carbonic anhydride passed through the solution to precipitate the alicylic base. The resulting carbonate is purified by reconverting into the base and reprecipitating with carbonic anhydride or, better, by dissolving in very dilute hydrochloric acid, treating the solution with a little sodium nitrite, and extracting the nitrosamine of the aromatic base, which is precipitated as a yellowish oil, with ether. If a small quantity of the purified carbonate gives a coloration with diazobenzenesulphonic acid the process is repeated, if not the base is isolated, dried over potash and barium oxide, and distilled. The yield is 35—40 per cent.

It is a colourless, mobile oil boiling at 267° (724 mm.; 153°, 23 mm.) without decomposition, and readily volatile with steam. It has an ammoniacal piperidine-like smell, a strongly alkaline reaction, a great affinity for carbonic anhydride, and the peculiar physiological action of the alicylic β-bases. (Compare Bamberger and Filehne, *loc. cit.*) It dissolves freely in organic solvents, but is only sparingly soluble in water, from which it separates as an oil on adding soda. A solution of the hydrochloride gives no coloration with ferric chloride in the cold, but on warming it turns a deep reddish-brown. The *hydrochloride*, $C_{10}H_{11}\cdot NHEt,HCl$, crystallises from water in anhydrous prisms, melts at 223·5°, and is readily soluble in water, alcohol, and chloroform, but only sparingly in hydrochloric acid, and insoluble in light petroleum. The *nitrate*, $C_{10}H_{11}\cdot NHEt,HNO_3$, is precipitated when nitric acid is added to an aqueous solution of the hydrochloride or to an ethereal solution of the base; it crystallises from hot water in needles or plates melting at 184°. The *nitrite*, $C_{10}H_{11}\cdot NHEt,HNO_2$, is precipitated when nitrous anhydride is passed into a well-cooled, ethereal solution of the base. It crystallises from water in long needles, melts at 180°, and is not decomposed by cold, very dilute acids or boiling water. The *picrate*, $C_{10}H_{11}\cdot NHEt,C_6H_3N_3O_7$, prepared by dissolving the base in a boiling, aqueous solution of picric acid, crystallises in long, orange-red needles, melts at 183·5°, and is readily soluble in water and alcohol. The *platinochloride*, $(C_{10}H_{11}\cdot NHEt)_2,H_2PtCl_6$, separates from boiling water in orange-yellow, stellate crystals melting at 204°. The *oxalate* crystallises from water in needles, the *carbonate* crystallises in small, colourless, deliquescent needles. The *acetyl*-derivative, $C_{10}H_{11}\cdot NAcEt$, prepared by digesting the base with acetic anhydride and sodium acetate, is a colourless oil boiling at 328° (718 mm.) without decomposition; it does not combine with bromine when treated therewith in chloroform solution. (Compare Bamberger and Lodter, Abstr., 1888, 604.)

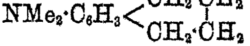
The *nitrosamine*, $C_{10}H_{11}\cdot NEt\cdot NO$, is best prepared by treating a strong hydrochloric acid solution of the base with sodium nitrite in a closed vessel, as in very dilute solutions no reaction occurs at the ordinary temperature; it separates slowly from the cold solution, but immediately on warming, as a yellowish oil which is only sparingly soluble in hot or cold water, and very slightly volatile with steam. It gives Liebermann's reaction, but only slightly.

Diazobenzene-ethyl-β-tetrahydronaphthylamine, $N_2Ph\cdot NEt\cdot C_{10}H_{11}$, separates in sulphur-yellow needles, together with pale-yellow crystals of tetrahydroethylnaphthylamine nitrate when the base (1 mol.) is suspended in ice-cold water, treated with a well-cooled solution of diazobenzene nitrate (1 mol.) and the mixture kept for some time at 0°; the diazoamido-compound is extracted with ether, the solution evaporated, and the residual reddish-brown oil placed in a freezing mixture. It crystallises in sulphur-yellow, hexagonal plates, melts at 58°, and is decomposed when warmed with acids. It imparts a red coloration to melted resorcinol. The *picrate*, $C_{16}H_{21}N_3,C_6H_3N_3O_7$, prepared by treating the diazoamido-compound with picric acid in ethereal solution, crystallises in ruby-red needles, and is readily soluble in alcohol but insoluble in ether. It decomposes on exposure to the light or when heated at about 100°.

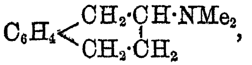
That β-tetrahydro-ethylnaphthylamine has the constitution assigned to it above follows from previous experiments and is also proved by the existence of the isomeric aromatic base. When the alicylic base is oxidised with potassium permanganate, as previously described in the case of the alicylic β-tetrahydronaphthylamine (Bamberger and Müller, Abstr., 1888, 712), it yields an oily acid the barium salt of which crystallises well, and is readily soluble in water; the acid itself could not be obtained in crystals, and is probably a mixture.

Ethyl-β-tetrahydronaphthylamine,  $\mathrm{NHEt{\cdot}C_6H_3}<\begin{array}{l}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}$ (aromatic), is formed in small quantities (4 per cent. of the base employed) when ethyl-β-naphthylamine is reduced as described above; it is isolated by evaporating the light petroleum mother-liquors from the alicylic base and purified by drying over barium oxide and fractionating. It is a colourless, neutral, mobile oil, boils at 291·5° (724 mm.), is volatile with steam, and dissolves freely in organic solvents, but is only sparingly soluble in water, and insoluble in soda. It combines immediately with nitrous acid, yielding an oily nitrosamine which gives Liebermann's reaction and forms dyes with diazo-compounds; the compound obtained with paradiazobenzenesulphonic acid is bright scarlet. In aqueous solutions of the hydrochloride ferric chloride produces no coloration, but on warming a reddish-brown precipitate is formed. Potassium dichromate and sulphuric acid have no action in the cold; on warming the solution becomes reddish-brown, but the colour disappears on continued boiling. The *hydrochloride* crystallises in anhydrous needles, melts at 173·5°, and is readily soluble in water, but is precipitated from the solution in nacreous plates on adding concentrated hydrochloric acid. In aqueous solution, an ammoniacal solution of silver nitrate produces a white, flocculent precipitate which gradually darkens on boiling, the solution turning red. The *platinochloride* crystallises in small, anhydrous, yellow needles, and is sparingly soluble in cold water; it is decomposed slowly by cold, but immediately by hot water. When the aromatic base is oxidised with potassium permanganate, adipic acid is formed, and the odour of carbylamine is distinctly perceptible.

Dimethyl-β-naphthylamine is best prepared by heating β-naphthylamine with methyl iodide and soda at 120° for several hours, and decomposing the resulting ammonium iodide by distilling with potash or by boiling with amyl alcoholic soda.

Dimethyl-β-tetrahydronaphthylamine,  $\mathrm{NMe_2{\cdot}C_6H_3}<\begin{array}{l}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}$ (aromatic), is formed together with very small quantities of the isomeric alicylic base when dimethyl-β-naphthylamine or the methiodide is reduced with sodium and amyl alcohol; the two products are separated by precipitating with carbonic anhydride as described above. It is a colourless, mobile oil, boils at 287° (718 mm.; 168°, 695 mm.) without decomposition, and is very similar to the corresponding ethyl-derivative. When an aqueous solution of the hydrochloride is warmed with auric chloride, gold is immediately precipitated; alcoholic solutions of the base precipitate silver from a solution of the nitrate even in the cold. The *hydrochloride*, $C_{10}H_{11}{\cdot}NMe_2,HCl$, separates in colourless, very deliquescent crystals when hydrogen chloride is passed into an ethereal solution of the base. In warm, aqueous solutions of this salt ferric chloride produces a turbidity and a yellow coloration; a mixture of sulphuric acid and potassium dichromate gives a yellow precipitate and, on warming, the solution turns a dirty-green. The *platinochloride*, $(C_{10}H_{11}{\cdot}NMe_2)_2,H_2PtCl_6$, is a yellow, crystalline compound, and is decomposed by boiling water. The *picrate* crystallises from warm water in needles. The *ferrocyanide* is a yellowish-white, crystalline compound, and is decomposed by boiling water. The *mercurochloride* crystallises in small plates or long needles, melts at 127·5°, and is readily soluble in hot, but only very sparingly in cold water. When the base is oxidised with potassium permanganate, it yields adipic acid.

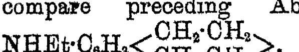
Dimethyl-β-tetrahydronaphthylamine (alicylic),



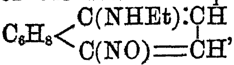
$$C_6H_4<\begin{matrix}CH_2\cdot CH\cdot NMe_2\\ CH_2\cdot CH_2\end{matrix},$$

boils at 166·5° (22 mm.), and resembles the corresponding ethyl base in reactions and properties. Its physiological action is similar to, but stronger than, that of tetrahydronaphthylamine. The *hydrochloride* crystallises in long needles, and is readily soluble in water. The *platinochloride* crystallises from water in orange-yellow needles, and is not decomposed by boiling water.

When paratolyl-β-naphthylamine is treated with sodium and amyl alcohol, a large quantity of resinous compounds is formed from which small quantities of a reduced base can be extracted by boiling with dilute mineral acids. This compound crystallises from hot water in colourless plates, melts at 44°, boils at 93° (18 mm.), and is very readily soluble in hot water. It is exceedingly volatile, and has the peculiar piperidine smell of the alicylic bases, but at the same time a distinct odour of narcissus. F. S. K.

Reduction of Secondary and Tertiary Alkyl-α-naphthylamines. By E. BAMBERGER and H. HELWIG (*Ber.*, **22**, 1311—1317; compare preceding Abstract).—*Ethyl-α-tetrahydronaphthylamine*,  $NHEt\cdot C_6H_3<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>$, is obtained when ethyl-α-naphthylamine (b. p. 303°, 722·5 mm.) is reduced with sodium and amyl alcohol, but no isomeric alicylic base is formed in the reaction. It is a colourless, neutral, mobile oil, boils at 286—287° (17 mm.), and is readily soluble in organic solvents but only sparingly in water and soda. It reduces warm alcoholic solutions of silver nitrate and gives an orange-red dye with diazobenzenesulphonic acid. In warm solutions of the hydrochloride, ferric chloride produces a wine-red and then a greenish-yellow coloration; potassium dichromate and sulphuric acid give a dirty yellow precipitate in the cold, but in hot solutions first a red and then a greenish-brown coloration is produced, and on adding more dichromate, a black, flocculent precipitate is formed. The *hydrochloride*, $C_{10}H_{11}\cdot NHEt,HCl$, crystallises from water in thick prisms or needles which effloresce at 80—90° and melt at 118°. The *platinochloride*, $(C_{10}H_{11}\cdot NHEt)_2,H_2PtCl_6$, crystallises in golden plates, is sparingly soluble in cold, and is decomposed by hot water. The *nitroso*-compound, $C_{10}H_{11}\cdot NEt\cdot NO$, separates as an oil when a hydrochloric acid solution of the base is treated with sodium nitrite; it gives Liebermann's reaction and is reconverted into tetrahydroethylnaphthylamine when warmed with tin and hydrochloric acid.

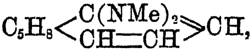
Paranitrosoethyltetrahydronaphthylamine hydrochloride separates in golden prisms or needles when an alcoholic hydrochloric acid solution of the nitroso-compound is kept for some time. The free *base*,



$C_6H_8<\begin{matrix}C(NHEt){:}CH\\ \quad\ |\\ C(NO){=\!=}CH\end{matrix}$, crystallises from boiling water in golden needles, melts at 119°, and is converted into tetrahydroparanaphthylenediamine when reduced with zinc-dust and hydrochloric acid.

When ethyltetrahydronaphthylamine is oxidised with potassium permanganate it yields adipic acid and oxalic acid.

Dimethyl-α-tetrahydronaphthylamine,



$C_5H_8<\begin{matrix}C(NMe)_2\\ CH{=\!=}CH\end{matrix}>CH$, prepared by reducing dimethyl-α-naphthylamine (b. p. 274·5°, 711 mm.) with sodium and amyl alcohol, is a colourless, mobile oil, which boils at 261—262° (721 mm.), turns brown on exposure to the air, and reduces ammoniacal silver nitrate solution. It gives coloured compounds with paradiazobenzenesulphonic acid; the *sodium* salt, $SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_{10}{\cdot}NMe_2$, crystallises in yellow plates. In warm acid solutions ferric chloride gives a red coloration which disappears on continued heating; potassium dichromate and sulphuric acid produce in the cold a dirty yellow precipitate, but in hot solutions a brownish-black precipitate is formed and the colour changes to brown. The *hydrochloride* is a syrup. The *platinochloride*,

$$(C_{10}H_{11}{\cdot}NMe_2)_2,H_2PtCl_6,$$

is an orange-yellow, crystalline compound, only moderately soluble in cold, and decomposed by hot water. The *methiodide*, $C_{10}H_{11}{\cdot}NMe_3I$, prepared by heating the base with methyl iodide at 90—100°, crystallises from water in prisms, melts at 164·5°, and is readily soluble in alcohol and hot water but only sparingly in cold water. The nitroso-derivative is an unstable oil.

When dimethyl-α-tetrahydronaphthylamine is oxidised with potassium permanganate, it yields adipic acid. F. S. K.

Hydrogenation of 1 : 2- and 1 : 4-Naphthylenediamines. Preparation of 2 : 2′-Naphthylenediamine.

By E. Bamberger and W. J. Schieffelin (*Ber.*, **22**, 1374—1384).—1 : 2-Naphthylenediamine (Lawson, Abstr., 1885, 1238) can readily be prepared by adding zinc-dust to a solution of phenylazo-β-naphthylamine in acetic acid until the colour changes to a bright yellow, filtering the hot solution into dilute sulphuric acid, and decomposing the sparingly soluble sulphate with hot soda solution. The yield amounts to about 78 per cent. of that theoretically possible.

Phenylamidonaphthylcarbamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}NH_2$, is a granular, crystalline powder, and melts above 335°: *naphthylenediphenylcarbamide*, $C_{10}H_6(NH{\cdot}CO{\cdot}NHPh)_2$, is very sparingly soluble in alcohol, carbon bisulphide, ether, and benzene; *naphthylenediphenyldithiocarbamide* forms pale yellow needles which melt at about 355—360° with decomposition. On hydrogenation, 1 : 2-naphthylenediamine yields two tetrahydro-bases, the "aromatic" base (compare this vol., p. 717) being the chief product.

Ar. tetrahydro-1 : 2-*naphthylenediamine*, $C_{10}H_{10}(NH_2)_2$, crystallises in flat, silky needles, melts at 84°, boils without decomposition at 220° under a pressure of 81 mm., and is readily soluble in alcohol, ether, and hot water. It exhibits all the properties of the "aromatic" hydro-bases, reduces solutions of platinum chloride and silver nitrate with the formation of metallic platinum and silver respectively, yields a carmine-red solution on treatment with ferric chloride in the cold, forms a deep bordeaux-red solution by the action of potassium dichromate and sulphuric acid in the cold, and on oxidation with potassium permanganate yields adipic and oxalic acids (compare Bamberger and Althausse, Abstr., 1888, 960). The salts are more soluble in water than those of 1 : 2-naphthylenediamine; the *hydrochloride*, $C_{10}H_{10}(NH_2)_2,2HCl$, crystallises in lustrous tabular forms and melts at about 260° with decomposition; the *nitrate*, $C_{10}H_{10}(NH_2)_2,2HNO_3$, crystallises in satiny scales, is somewhat sparingly soluble in water, and melts at 201°. The *diacetyl*-derivative, $C_{10}H_{10}(NHAc)_2$, crystallises in silky, matted needles, melts at 245°, is readily soluble in chloroform and alcohol, sparingly soluble in ether, light petroleum, and cold water, and is not acted on by bromine.

Ac. tetrahydro-1 : 2-*naphthylenediamine* is chiefly found in the aqueous layer obtained when the reduction product is poured into water (compare Bamberger and Müller, Abstr., 1888, 599), and is separated by concentrating the acidified aqueous solution, precipitating the base in the cold with aqueous soda, extracting it with ether, and precipitating it from the ethereal solution as carbonate; the process being repeated until the base is free from admixture with the "aromatic" isomeride. Owing to the very small quantity obtained, an analysis of the base could not be made. It has all the properties of an "alicyclic" tetrahydro-base, and forms a platinochloride crystallising in golden-yellow needles.

Ar. tetrahydro-1 : 4-*naphthylenediamine* is the sole product formed on reducing 1 : 4-naphthylenediamine. Its hydrochloride is a snow-white, glittering, crystalline powder, which melts above 360°, and in the moist state rapidly becomes green on exposure to the air. The base is obtained as an oil on treating the hydrochloride with alkalis; it distils without decomposition under a pressure of 20 mm. and solidifies, on cooling the receiver, to a mass of white, needle-like crystals which, on exposure to the air, rapidly become coloured and finally resinified. In its reactions it exhibits the properties of an "aromatic" tetrahydro-base, and on oxidation with potassium permanganate yields adipic and oxalic salts. The *diacetyl*-derivative, $C_{10}H_{10}(NHAc)_2$, crystallises in long, white, silky needles, melts at 285°, is sparingly soluble in water, chloroform, and ether, and is not acted on by bromine.

Diacetyl-1 : 4-*naphthylenediamine* forms lustrous, white needles, melting at 305°, and is identical with Kleeman's diaceto-α-naphthylenediamine (Abstr., 1886, 472).

2 : 2′-*Naphthylenediamine* can be prepared by heating 2 : 2′-dihydroxynaphthalene with four times its weight of ammonium calcium chloride at 260—270° for eight hours (compare Lange, *Chem. Zeit.*, 1888, 856). It crystallises in white, satiny scales, and melts at 159°.

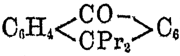
W. P. W.

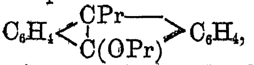
β-Dinaphthylparaphenylenediamine and its Derivatives. By L. RUEFF (*Ber.*, **22**, 1080—1083).—*β-Dinaphthylparaphenylenediamine*, $C_6H_4(NH{\cdot}C_{10}H_7)_2$, is obtained when paraphenylenediamine is heated at 200° with excess of β-naphthol. It is best crystallised from boiling aniline, and forms white scales soluble in glacial acetic acid, cumene, and nitrobenzene, almost insoluble in alcohol, ether, or benzene. It melts at 235°, and boils in a vacuum at 400° with slight decomposition. It is scarcely attacked by dilute acids; strong sulphuric acid dissolves it, and on the addition of potassium nitrate or nitrite the solution (like that of the corresponding diparatolyl-compound) turns greenish-violet, and then an intense blue. The *picrate*, $C_6H_4(NH{\cdot}C_{10}H_7),2C_6H_2(NO_2)_3{\cdot}OH$, forms glistening, black needles, soluble in boiling benzene and melting at 217°. The *dimethyl*-derivative, $C_6H_4(NMe{\cdot}C_{10}H_7)_2$, yields white scales which dissolve in boiling benzene and melt at 180°. The *diacetyl*-derivative forms small, white scales soluble in boiling benzene, melts at 210° and chars when strongly heated. The *dibenzoyl*-derivative crystallises in white scales, melts at 220° and is soluble in boiling benzene. L. T. T.

β-Bromonaphthalenesulphonic Acids. By S. FORSLING (*Ber.*, **22**, 1400—1403).—2 : 3′-*Bromonaphthalenesulphonic acid* (compare Houlding, Proc., 1889, 74) can be prepared by Sandmeyer's method from the Brönner β-naphthylamine-β-sulphonic acid. The *potassium* salt, with ½ mol. H_2O, forms a microcrystalline powder; the *ammonium*, *barium*, and *silver* salts were also prepared. The *bromide*, $C_{10}H_6Br{\cdot}SO_2Br$, crystallises from benzene in pale-yellow aggregates of small needles, melts at 118°, and is readily soluble in benzene and chloroform, sparingly soluble in ether and light petroleum; the *amide* crystallises in long, slender needles, and melts at 207°. The dibromonaphthalene, obtained by distilling the bromide with phosphorus pentabromide, crystallises from a mixture of ether and chloroform in four-sided, colourless tables, melts at 158°, and is sparingly soluble in alcohol, readily soluble in ether, chloroform, and light petroleum. It is undoubtedly identical with the ε-dibromonaphthalene (m. p. 159·5°) of Jolin, and the author suggests that its formation under the conditions given by Jolin was due to the presence of some β-bromonaphthalene in the α-bromonaphthalene employed.

2 : 1′-*Bromonaphthalenesulphonic acid* can be prepared in like manner from the Badische β-naphthylamine-α-sulphonic acid. Its *potassium* salt crystallises with 1 mol. H_2O. The *bromide* crystallises from chloroform in broad needles, melts at 151°, and is readily soluble in benzene and chloroform. The corresponding dibromonaphthalene crystallises in small, white needles, melts at 75°, is sparingly soluble in alcohol, readily soluble in ether and chloroform, and is identical with that obtained by Meldola (Trans., 1885, 497), and by Darmstädter and Wichelhaus (*Annalen*, **152**, 298). W. P. W.

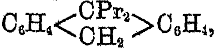
Propyl-derivatives of Anthranol. By F. HALLGARTEN (*Ber.*, **22**, 1069—1072; compare Abstr., 1888, 1202).—*Dipropylanthrone*,

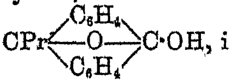
 $C_6H_4{<}\genfrac{}{}{0pt}{}{CO-}{CPr_2}{>}C_6H_4$, is obtained, together with propylanthranyl propyl other, when an aqueous (25 c.c.) solution of anthranol (5 grams) and potash (5 grams) is boiled for four hours with propyl iodide (12—13 grams). The resulting syrup is extracted with boiling water and then mixed with light petroleum, whereon dipropylanthrone is precipitated in yellowish crystals. It separates from benzene and light petroleum in almost colourless, rhombic crystals, melts at 124°, and is soluble in glacial acetic acid, ether, benzene, and hot alcohol, but only sparingly in light petroleum, and insoluble in alkalis. When oxidised with chromic acid in glacial acetic acid solution, it yields considerable quantities of anthraquinone.

Propylanthryl propyl ether,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CPr—}{C(OPr)}{>}C_6H_4$, remains in the mother-liquors after precipitating the dipropylanthrone with light petroleum. The solution is evaporated, the residue dried at 120°, dissolved in a small quantity of absolute alcohol, and precipitated with a hot, concentrated alcoholic solution of picric acid. The violet precipitate is repeatedly boiled with ammonia and the colourless residue recrystallised from alcohol, from which it separates in small, yellowish needles, melting at 72°. It is soluble in light petroleum, benzene, ether, and alcohol, but insoluble in alkalis. When oxidised with chromic acid, it yields anthraquinone. The *picrate*,

$$C_{20}H_{22}O,C_6H_3N_3O_7,$$

crystallises from alcohol and is decomposed when heated at 90—100°.

Dipropylanthracene dihydride,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CPr_2}{CH_2}{>}C_6H_4$, is prepared by heating dipropylanthrone at 140—170° with hydriodic acid and amorphous phosphorus. It crystallises from alcohol in colourless plates, softens at 46—47°, is soluble in all ordinary solvents except water, forming fluorescent solutions, and dissolves in concentrated sulphuric acid with a yellow coloration.

Propyloxanthranol,  $CPr\begin{array}{c}C_6H_4\\ —O— \\ C_6H_4\end{array}C\cdot OH$, is obtained when propylanthranyl propyl ether is oxidised with a cold dilute solution of chromic acid. It can also be prepared by heating anthraquinone (20 grams) with zinc-dust (40 grams), potash (30 grams), propyl iodide (40 grams), and water (1000 c.c.), boiling the product with water, and extracting the dried residue with 40 per cent. alcohol. It separates from alcohol in colourless crystals, melts at 164°, and is readily soluble in benzene and glacial acetic acid, but only sparingly in ether, and insoluble in alkalis and light petroleum. It dissolves in concentrated sulphuric acid with a yellowish-red coloration.

F. S. K.

Action of Heat and Acetic Acid on French Essence of Terebenthene. By G. BOUCHARDAT and LAFONT (*Ann. Chim. Phys.* [6], **16**, 236—262; compare Abstr., 1886, 475).—A sample of essence of terebenthene (b. p. 155—158°), which rotated the plane of polarisation

−32° 52′ ($l = 10$ cm.), was mixed with glacial acetic acid (1·5 vols.) and heated at 100° in a sealed tube previously filled with carbonic anhydride. An optical examination of samples taken from time to time showed that the rotatory power, which in the freshly prepared mixture was −6° 50′ ($l = 5$ cm.), increased in the course of 97½ hours to −9° 35′, and tended towards a limit of about −10°, but even after 97 hours only half the hydrocarbon had combined with the acid. The contradictory results arrived at by Berthelot (*Ann. Chim. Phys.* [3], **38**, 44) are probably due to some difference in the essence employed. The commercial substance is prepared by distilling the resin in presence of acetic acid and resinous acids; in this process it undergoes modification and, as the rotatory power of the products which are first formed is always higher than that of the non-modified essence, any further change results in a diminution of optical activity. The modified essence also contains an active terpilene, the rotatory power of which diminishes gradually when it is heated at 100° with acetic acid.

When similar mixtures of essence of terebenthene and acetic acid are heated at 150° and 200°, the rotatory power first increases for a very short time, then rapidly diminishes, and finally the solution becomes inactive.

If in the experiments at 100° a trace of sulphuric acid is added to the mixture, the rotatory power quickly reaches a maximum, and the more quickly the more sulphuric acid added, it then decreases rapidly, and finally the solution becomes slightly dextrorotatory.

A sample of essence of terebenthene (800 grams), which rotated the plane of polarisation −16° 26′ ($l = 5$ cm.), was mixed with glacial acetic acid (1600 grams) and the mixture, the rotatory power of which was −7° 4′, heated at 100° for 64 hours, a stream of carbonic anhydride being passed during the whole operation. The rotatory power increased to −9° 20′, and after keeping at the ordinary temperature for two months longer it attained −9° 28′. The crude product was washed with water, and the residue (about 1000 grams) submitted to fractional distillation, first under the ordinary and then under reduced pressure. The boiling point, rotatory power, and weight of the various fractions obtained are given in a table. The products were, firstly, unchanged terebenthene of specific rotatory power $[\alpha]_D = -49° 1'$, the hydrochloride of which is solid and has the specific rotatory power $[\alpha]_D = -13° 3'$. The high specific rotatory power of the hydrocarbon may be due to the presence of active camphene. The hydrochloride is quickly decomposed by water (50 vols.) at 100°, but equilibrium is almost established after seven hours; 47 per cent. of the salt has then been decomposed, and the solution contains camphene of rotatory power −31°. It was proved by an experiment with very active (−80°) camphene, that the rotatory power is diminished by about one-fourth by converting into the hydrochloride and boiling the latter with alcoholic potash; assuming a proportionate reduction in the above case, it would follow that the rotatory power of the unchanged terebenthene is increased by contact with acetic acid independently of the formation of camphene.

The second product is a terpilene, boiling at 178°, which has the rotatory power $[\alpha]_D = -80·5°$, and has all the chemical properties of dextrorotatory citrene.

The next products are various acetates of camphenols having the same composition but different rotatory powers; the dextrorotatory ($[\alpha]_D = 12°$ approx.) boil at a lower temperature than the lævorotatory compounds, the rotatory power of which may be as much as −35°. It is almost impossible to separate the acetates by fractional distillation, as the difference in their boiling points is only about 10°, but, when treated with alcoholic potash at 100° they are converted into the corresponding dextro- and lævo-camphenols (borneols), which can be separated by fractional distillation or fractional crystallisation, as the lævo-compounds crystallise more readily and boil at a higher temperature than the dextrorotatory compounds. The rotatory power of the lævo-camphenols, in 10 per cent. alcoholic solution at about 18°, varied in the different fractions from −33° 20′ to −25° 20′, and was on the average −31° to −32°; the products of greatest activity are obtained from the higher boiling acetates, or from the fractions of the higher boiling camphenols. The differences in rotatory power of the various lævo-borneol fractions seem to be due to [illegible] presence of a little dextro-borneol or dextro-camphenol, perhaps also to traces of terpilenol; as the mean value is the same as that of various natural lævo-borneols, it follows that the treatment at 100° has not sensibly modified the rotatory power of this substance, nor that of the ethereal salts from which it is derived. The solid camphor, obtained by oxidising these borneols, has the specific rotatory power $[\alpha]_D = -40°$ in 10 per cent. solution.

The dextro-camphenol was isolated from the mother-liquors from the lævo-compound, and obtained in an almost pure condition by crystallising at a low temperature. It begins to melt at about 50° and boils at 195°, or about 10° lower than the lævo-compound; its rotatory power is, on the average, $[\alpha]_D = 9° 20′$, but it probably contains lævo-camphenol. It does not seem to correspond with the dextrorotatory acetates, and probably a small portion of the latter are reconverted into the lævo-compound during hydrolysis. When treated with nitric acid, it yields a compound having the same composition as Japan camphor, but it is not acted on as readily as the lævo-camphenol. This camphor solidifies at a very low temperature, boils at 195°, and is very readily soluble in alcohol, ether, and light petroleum; its specific rotatory power is about $[\alpha]_D = -57°$. The properties of the dextro-borneols described above seem to show their connection with the camphenol of variable lævorotatory power discovered by Montgolfier.

The fourth product of the action of acetic acid on essence of terebenthene is an acetate which yields a lævo-terpilenol melting at 33°, boiling at 218°, and of specific rotatory power $[\alpha]_D = -86° 38′$.

The products obtained by heating similar mixtures of essence of terebenthene and acetic acid at 150° for 64 hours, and at 200° for 12 hours, were examined in the same way. In the experiment at 150° the crude product from 1400 grams of the mixture weighed 550 grams, and its rotatory power was −8° 40′ ($l = 10$ cm.); the product obtained at 200° only rotated the plane of polarisation −40′. Although the mixtures themselves are so feebly active, the various fractions have considerable rotatory powers, some being dextro- some lævo-rotatory. At 150° or 200° no terebenthene remains unchanged, and the most volatile fractions consist of camphene of feeble activity. The crystalline hydrochloride of the portion boiling at 160—167° is dextrorotatory, a fact which indicates the presence of lævo-camphene, $[\alpha]_D = -8° 20'$; it is quickly decomposed by water at 100°, and the camphene obtained is crystalline. Terpilene of sp. gr. 0·8647 is formed in large quantities in both cases, but at the higher temperature the product is less active. The fractions passing over above 100° under diminished pressure, consist of dextro- and lævo-rotatory acetates of camphenols and contain no trace of terpilenol, the acetates of terpilene, which are doubtless formed, having been destroyed again and converted into terpilene. The dextro-camphenol acetates, just as in the experiment at 100°, do not yield an equivalent quantity of dextro-borneol, but there is a partial return to the stable lævorotatory type. The rotatory powers of the lævo-borneols and of the lævo-camphors derived therefrom are considerably less than those of the corresponding compounds obtained in the experiments at 100°.

The above experiments prove that the products obtained at 100° are the same, and exist in the same proportions, and have the same rotatory powers as those obtained in the cold, but the action takes place much more quickly. A higher temperature diminishes the rotatory powers, especially as regards the isomeric hydrocarbons formed, and increase of temperature has more effect than a prolongation of the time during which the reaction takes place. The borneols obtained by heating at 150° for 64 hours have only about one-third the rotatory power of those produced in 12 hours at 200°; this anomaly depends on the formation of unstable dextro-camphenol. The camphor derived from the camphenol which is obtained at 150° is more active than that derived from the corresponding compound produced at 200°, a fact which seems to show that the formation of substances intrinsically inactive, or inactive by compensation, is a direct effect of increase of temperature. The diminution in rotatory power of the camphors and modified hydrocarbons seems to be due to the formation of substances inactive, *per se*, or inactive by compensation. At temperatures above 150°, terpilenol and its acetates are destroyed as fast as they are formed, yielding a terpilene which is less and less active. F. S. K.

Mesocamphoric Acid. By C. Friedel (*Compt. rend.*, **108**, 978—984).—Mesocamphoric acid is an isomeride of camphoric acid, obtained, according to Wreden, by heating camphoric acid with hydriodic or hydrochloric acid, and readily converted by boiling with dilute hydrochloric acid into an inactive acid, agreeing in other properties with the dextrogyrate acid (this Journal, 1872, 146). Jungfleisch obtained the same acid by heating camphoric acid with water only, paracamphoric acid being formed at the same time (*Bull. Soc. Chim.*, **19**, 530).

The author prepared a considerable quantity of this acid, partly by the action of hydriodic acid on the dextrogyrate acid, but mainly by the action of heat on the latter in presence of water or very dilute hydrochloric acid. When the product is crystallised it yields, first unaltered camphoric acid, then small, hard, brilliant crystals of a new modification, which the author terms provisionally isocamphoric acid, and lastly mesocamphoric acid.

Isocamphoric acid melts at 172·5°, and crystallises in small octahedra with a square base, modified by faces of the prism on the angles, and by other faces; $a^1\,a^1 = 62^\circ\,50'$; $b^{\frac{1}{2}}\,b^{\frac{1}{2}} = 45^\circ\,45'$: optical examination shows that the crystals belong to the quadratic system. When crystallisation takes place very slowly, isocamphoric acid forms rhombic lamellæ belonging to the rhombic system, but if these are allowed to remain in the mother-liquor, or if they are recrystallised, they change into quadratic octahedra. It follows that isocamphoric acid is dimorphous; both forms are anhydrous, and melt at the same temperature. Isocamphoric acid is dibasic, and, like all hydroxy-acids, gives no distinct reaction with Poirrier's orange. It is less soluble than camphoric acid; 100 parts of water at 15·5° dissolve only 0·38 gram. It is quite distinct from the ordinary lævogyrate acid, but its rotatory power is equal and opposite to that of the dextrogyrate acid; in alcoholic solution, $[\alpha]_D = -46^\circ$.

If the mother-liquor from isocamphoric acid is allowed to remain, it gradually becomes capable of depositing a further quantity of the ordinary dextrogyrate acid. This is readily separated by taking advantage of the fact that all the camphoric acids readily form supersaturated solutions, and the crystallisation of any one of them can be determined by introducing crystals of the same kind. Mesocamphoric acid can then be obtained from the liquid, but if it is recrystallised once or twice, it yields more isocamphoric acid, and the same set of changes can be repeated time after time, the proportion of mesocamphoric acid gradually decreasing. It follows from these observations that mesocamphoric acid is a mixture of the dextrogyrate acid with a lævogyrate acid having an equal but opposite rotatory power and differing also in other physical properties. Mesocamphoric acid can in fact be obtained by mixing equivalent quantities of dextrogyrate camphoric acid and isocamphoric acid. The product is optically inactive, but its gradual resolution by repeated recrystallisation can be followed with the polarimeter.

If camphoric acid is heated for 48 hours at 180—190° with one-tenth its weight of water, the solution becomes inactive, and if the liquid contains 50 parts of water to one of acid it first deposits a lævogyrate acid, and afterwards some ordinary camphoric acid, which, however, is very difficult to separate from the mesocamphoric acid which accompanies it. Isocamphoric acid treated in the same way yields mesocamphoric acid.

It is evident from these results that mesocamphoric acid belongs to the same group as racemic acid.

When isocamphoric acid is distilled, it yields an anhydride which melts at 221°, boils without decomposition, and crystallises from alcohol in silky needles. When the solution is slowly concentrated by evaporation, it yields crystals which seem to belong to the rhombic system. It is optically inactive. When heated with potassium hydroxide, it is converted into the dextrogyrate acid. C. H. B.

Action of Ozone on Guaiacum Resin. By N. KOWALEWSKY (*Chem. Centr.*, 1889, 289—290, from *Centr. Med. Wiss.*, **27**, 66—68).—Ozone forms not only a blue oxidation product by its action on guaiacum resin, but also a whole series of coloured products. The colours do not all appear at the same time, but in a certain order, the blue standing about the middle of the series. If damp guaiacum resin is besmeared with old turpentine and brought near the Babo apparatus, the paper commences to smoke, without any appearance of the colours. Ozone has no action on perfectly dry guaiacum resin. If a small piece of iodine is placed on damp guaiacum paper, a blue ring forms all round, which is strengthened by being moistened with water. This reaction is extremely delicate. J. W. L.

Tanghinin, from Tanghinia Venenifera. By ARNAUD (*Compt. rend.*, **108**, 1255—1257).—Tanghinin is the active principle of *tanghin*, the judicial poison of the Malgaches, which is extracted from the kernel of the fruit of *Tanghinia venenifera*, one of the Apocynaceæ.

The kernels contain about 75 per cent. of fat of a buttery consistence, part of which can be removed by pressure, and the remainder by carbon bisulphide, in which the tanghinin is insoluble. The residue is then extracted with boiling alcohol, and this on cooling deposits crystals of tanghinin, which is present in the kernels to the extent of 25 grams in 2·55 kilos. Tanghinin is a cardiac poison resembling strophantin and ouabaïn; it crystallises in colourless, anhydrous rhombs, which give no colour reactions, become pasty at 170°, melt at about 182°, and burn without residue at a higher temperature. Tanghinin is almost insoluble in water, but if left in contact with it for some hours, swells up and forms a thick mucilage containing microscopic crystals in suspension. It is, however, readily soluble in concentrated alcohol, and somewhat soluble in ether. In a saturated alcoholic solution at 20°, it has a lævorotatory power $[\alpha]_D = -67°$.

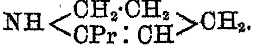
Tanghinin dried at 115° contains C, 65·74; H, 8·19; O, 26·07 = 100. It contains no nitrogen, and when treated with dilute acids yields a yellow product which cannot be crystallised from alcohol, and a small quantity of a very bitter substance, but no reducing sugar is formed. It follows that tanghinin is neither an alkaloïd nor a glucoside. C. H. B.

Xanthophyllidrin. By L. MACCHIATI (*Chem. Centr.*, 1889, 350, from *Nuovo. botan. Ital.*, **20**, 474—476).—After washing the leaves of *Evonymus japonica* with water and ether, and extracting with alcohol so as to separate the chlorophyllan, a yellow liquid was obtained by washing the latter with water, from which lemon-yellow crystals, insoluble in alcohol, ether, and benzene, were obtained. The author has named the substance *xanthophyllidrin*. It appears to accompany the chlorophyll constantly. J. W. L.

Behaviour of Pyrroline and its Derivatives as regards Raoult's Law. By G. MAGNANINI (*Zeit. physikal. Chem.*, 3, 347—350).—Pyrroline, like phenol, when examined by Raoult's method, gives values for the molecular weight which are too high in the case of a solution in benzene, but are normal for an acetic acid solution. The derivatives of pyrroline, whether examined in acetic acid or benzene solutions, give practically normal values, a slight rise being observed in each case with increasing concentration. The latter is particularly marked in the case of α-acetylpyrroline and the methyl salt of α-pyrrolinecarboxylic acid, as also for iodole (tetriodopyrroline), which on account of its slight solubility in acetic acid was examined in solution in ethylene dibromide. H. C.

Coniceïns. By E. LELLMAN (*Ber.*, **22**, 1000—1004).—The author and W. Geller have previously shown that the unstable, oily compound $C_5NH_{10}Cl$, which is formed when piperidine is treated with bleaching powder, is converted into a secondary piperideïne by treating with alcoholic potash. This secondary base only exists in the state of vapour, as at a lower temperature it immediately polymerises, with formation of a crystalline dipiperideïne.

α-Methylpiperidine and conine both yield colourless, oily, very unstable chloro-derivatives when boiled with bleaching powder. The compound $C_8NH_{16}Cl$, obtained from conine, when treated with alcoholic potash, yields an optically inactive secondary coniceïne (b. p. 171°), which is probably identical with the γ-coniceïne prepared by Hofmann (Abstr., 1885, 401 and 562), and has the constitution



$$NH<\begin{matrix}CH_2\cdot CH_2\\ CPr:CH\end{matrix}>CH_2.$$

F. S. K.

β-Ethyl-α-Stilbazole and its Derivatives. By G. PLATH (*Ber.*, **22**, 1057—1063).—The salts of β′-ethyl-α-stilbazoline (compare this vol., p. 163) cannot be obtained in a crystalline condition; the hydrochloride is poisonous.

The *dibromide*, $C_{15}H_{15}NBr_2$ (*loc. cit.*) separates from ether in nodular crystals, and from alcohol in small needles melting at 127·5—128°; it is soluble in benzene, chloroform, and carbon bisulphide. When heated with water at 130—140°, it yields ethylstilbazole and tarry products.

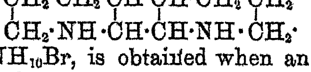
The *diacetate*, $C_{15}H_{15}N(OAc)_2$, was obtained in an impure condition by boiling the dibromide with silver acetate and glacial acetic acid; it is a bright-red, neutral, unstable oil, boils at 315—320° with decomposition, and is almost insoluble in water.

When ethylstilbazole is oxidised with a warm 2 per cent. solution of potassium permanganate, it is converted into benzoic acid and isocinchomeronic acid. F. S. K.

Piperideïne and Dipiperideïne. By E. LELLMANN and R. SCHWADERER (*Ber.*, **22**, 1318—1328, 1328—1336; compare Lellmann, Abstr., 1888, 970).—A dipiperideïne, $(C_5H_9N)_2$, is formed when chloropiperidine, prepared by the method described by Bally (*ibid.*, 964), is treated with alcoholic potash in the cold, but it is best obtained by gradually adding chloropiperidine to a boiling 10 per cent. solution of alcoholic potash. The alcohol is evaporated, the residue mixed with water, the brown, oily product extracted with ether and fractionated. The distillate gradually solidifies to a mass of well-defined crystals melting at 60—61°. Molecular weight determinations by Raoult's method in glacial acetic acid solution, and vapour-density determinations by V. Meyer's method at 200°, 230°, and 300°, show that at temperatures below 200° the molecular formula is $C_{10}H_{18}N_2$, but that between 200° and 230° dissociation commences. It has no constant boiling point, and within certain limits it can be distilled at almost any temperature by regulating the supply of heat. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, chloroform, and acids, but only very sparingly in water; cold dilute alkaline solutions become turbid on heating. It is slightly volatile with steam. Aqueous solutions give a gelatinous precipitate with zinc chloride, and with mercuric chloride a white precipitate which darkens on heating. A solution of the hydrochloride gives no reaction with platinic chloride, but auric chloride produces an oily precipitate. The *picrate* is an oil. Dipiperideïne is a secondary base, as is proved by the fact that it combines with acetic anhydride, but does not give the carbylamine reaction.

A compound, $C_{17}H_{23}N_3S$, is formed when dipiperideïne (10 grams) is dissolved in alcohol, treated with phenyl thiocarbimide (8·5 grams), and the solution kept for some time. It crystallises from alcohol in colourless needles, melts at 143—144° with decomposition, and is moderately soluble in dilute alcohol, but only sparingly in ether. It dissolves unchanged in cold, dilute hydrochloric acid, and the solution gives precipitates with mercuric and platinic chlorides; when heated with acids it is decomposed, and phenyl thiocarbimide is liberated. At 150° it is decomposed into aniline, and a compound, $C_{11}H_{16}N_2S$, which was not obtained in a pure state. This reaction shows that dipiperideïne contains two imido-groups. (Compare Lellman, Abstr., 1885, 976). When the compound $C_{17}H_{23}N_3S$ is heated with phenyl thiocarbimide at a moderately high temperature, thiocarbanilide is produced; the formation of this anilide seems to show that dipiperideïne combines with 2 mols. of phenyl thiocarbimide, but the compound is subsequently decomposed.

It follows from these experiments that dipiperideïne has most probably the constitution



$$\begin{array}{ccccccccccc} CH_2 & \cdot & CH_2 & \cdot & CH & \cdot & CH & \cdot & CH_2 & \cdot & CH_2 \\ | & & & & | & & | & & & & | \\ CH_2 & \cdot & NH & \cdot & CH & \cdot & CH & \cdot & NH & \cdot & CH_2 \end{array}.$$

A bromopiperidine, $C_5NH_{10}Br$, is obtained when an aqueous solution of piperidine is gradually added to a mixture of bromine (130 grams), calcium hydrate (300 grams), and water, a current of steam being passed through the mixture during the operation (compare Hofmann, Abstr., 1885, 401 and 562). The yellowish oil which collects in the receiver is washed with water to free it from piperidine, and dried over calcium chloride. It decomposes more quickly than the corresponding chloro-derivative, yielding colourless needles melting at 234°. When boiled with alcoholic potash, it is converted into a crystalline compound very similar to the dipiperideïne described above, but probably other bases are also formed in the reaction.

A colourless salt separates in crystals when a dilute hydrochloric acid solution of the dipiperideïne described above is evaporated over sulphuric acid. This compound, when dried over phosphoric anhydride, has the composition $C_5NH_9,HCl + H_2O$, and is most probably piperidine hydrochloride, as is shown by experiments described below. It softens and turns yellowish at 70°, loses its water at 120°, and melts at 150° when heated very carefully; when heated quickly it melts at about 80°. The molecular weight, determined by Raoult's method with glacial acetic acid and immediately after solution, was found to be 155, but the depression gradually increased.

Dipiperideïne hydrochloride remains as a yellow, amorphous, very hygroscopic salt, when a solution of the base (1 mol.) in very dilute hydrochloric acid (2 mols.) is evaporated over sulphuric acid.

Acetylpiperideïne, C_5NH_8Ac, is formed when dipiperideïne is boiled with acetic anhydride. It is a colourless oil, boils at 219·5—220·5°, and is readily soluble in all ordinary solvents except water. The molecular weight, determined in glacial acetic acid solution, was found to be 130·2. It is hydrolysed by boiling concentrated hydrochloric acid, and dipiperideïne is obtained when the resulting hydrochloride is decomposed with soda.

Di-paranitrobenzylpiperideïne, $(C_5NH_8 \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$, is formed when a benzene solution of dipiperideïne (2 grams) and paranitrobenzyl chloride (4·2 grams) is heated for a long time with an aqueous solution of sodium carbonate, the whole being frequently shaken. It crystallises from boiling alcohol in ruby-red needles, melting at 120·5°. The molecular weight determined in benzene solution was found to be 441. It is decomposed by cold dilute hydrochloric acid, and on adding ammonia to the solution, paranitrobenzylpiperideïne is precipitated. The last-named compound polymerises very readily, being reconverted into di-paranitrobenzylpiperideïne; this change takes place almost immediately when the simpler compound is treated with a little ether.

A compound, $C_{10}H_{16}N_2,CS_2$, is formed when dipiperideïne is boiled with carbon bisulphide. It crystallises in yellowish needles, melts at 150° with decomposition, and is readily soluble in alcohol, ether, and benzene; it forms a crystalline additive compound with benzene. It is not decomposed by cold, dilute hydrochloric acid, but is reconverted into dipiperideïne when heated with alkalis.

When dipiperideïne is warmed for a day with tin and concentrated hydrochloric acid, it is completely converted into piperidine; the same change occurs, but very much more slowly, when an alcoholic solution of dipiperideïne is treated with sodium amalgam at the ordinary temperature. F. S. K.

Polymerisation of Compounds containing Doubly-bound Carbon-atoms. By E. Lellmann (*Ber.*, 22, 1337—1341).—The author has compiled examples of the polymerisation of compounds containing doubly-bound carbon-atoms, amongst others the cases of piperideïne (compare preceding Abstract), pyrroline and isopropylpyrroline (Dennstedt, this vol., p. 400), and coniceïdine.

The so-called hydroquinoline, as was proved by molecular weight determinations in both benzene and glacial acetic acid solution, is in reality a hydrodiquinoline $(C_9H_9N)_2$. F. S. K.

Oxidation of α-Pipecoline. By H. BUNZEL (*Ber.*, **22**, 1053—1057).—In preparing α-pipecoline by Ladenburg's method (Abstr., 1885, 557) it is not necessary to purify the product by means of the nitrosamine as, after decomposing the sodium ethoxide with water, the pipecoline being readily volatile distils with the alcohol; the distillate contains only very small quantities of picoline and hydrocarbons, and the hydrochloride prepared therefrom is almost pure, so that, after decomposing the salt with potash and fractionating twice, the free base, boiling at 118—120°, is obtained in a pure state. 120 grams of α-picoline yield 96 grams of α-pipecoline.

Benzoylpipecoline, $C_6NH_{12}Bz$, is prepared by gradually adding benzoic chloride (30—35 grams) to a well-cooled mixture of pipecoline (20 grams), and 50 per cent. caustic soda (32 grams) with constant shaking, and, as soon as the reaction is at an end, adding water and warming. The product is extracted with ether, the solution washed with dilute soda, sulphuric acid, and water consecutively, dried, the ether evaporated, and the residue recrystallised from alcohol. It is a colourless compound melting at 44—45°, and is readily soluble in all solvents except water.

Benzoyl-δ-amidocaproic acid, $C_{13}H_{17}NO_3$, is formed when benzoylpipecoline (10 grams) is suspended in water (450 grams), the mixture warmed and treated with an aqueous (450 grams) solution of potassium permanganate (32—35 grams) in the course of 10 to 15 hours. The unchanged base is extracted with ether, the filtered solution acidified with sulphuric acid, and the precipitated acid recrystallised from water or ethyl acetate. The yield of the crude product is 50—75 per cent. of the benzoylpipecoline employed. It crystallises from hot water in long needles, melts at 148°, and is readily soluble in alcohol, moderately so in ethyl acetate, and insoluble in ether. When heated for three hours at 180° with concentrated hydrochloric acid, it is completely decomposed with separation of benzoic acid. The *zinc* salt, $(C_{13}H_{16}NO_3)_2Zn + H_2O$, crystallises from water in colourless needles melting at 212—213°, and gradually loses its water when kept over sulphuric acid under diminished pressure. The *silver* salt, $C_{13}H_{16}NO_3Ag$, separates in colourless, nodular crystals when a warm solution of the zinc salt is treated with silver nitrate. The *copper* salt is insoluble in water and is unstable. The *barium* salt is crystalline, but very readily soluble in water and absolute alcohol.

α'-Hydroxy-α-pipecoline, $C_6NH_{11}O$, is obtained when benzoylamidocaproic acid is distilled, the distillate boiled with soda, the solution extracted with chloroform, and the chloroform evaporated. It crystallises in plates, melts at 84°, and is readily soluble in all ordinary solvents, the solutions having a neutral reaction. F. S. K.

Formation of Colouring Matters from Paradiamidodiphenylpiperazine. By E. LELLMANN and C. SCHLEICH (*Ber.*, **22**, 1387—1389).—Diphenylpiperazine (compare Morley, Abstr., 1880, 112) is best prepared by warming 100 grams of aniline with an equal weight of ethylene bromide, and, after the vigorous reaction has taken place and the product become solid, adding 110 grams of ethylene bromide, heating the whole at 130—140° in a reflux apparatus, and slowly adding very concentrated aqueous potash in quantity sufficient to combine with the bromine; after heating for many hours, the excess of ethylene bromide is removed by steam distillation, and the solid residue washed with hot alcohol. The yield of pure diphenylpiperazine amounts to 90—100 grams from 100 grams of aniline. The paradiamido-derivative is best obtained by reducing the dinitroso-derivative by Morley's method.

When paradiamidodiphenylpiperazine hydrochloride is oxidised with two molecular proportions of phenol or naphthol by means of ferric chloride, a blue indophenol is obtained, and an indamine and saffranine are formed when it is mixed with two and four molecular proportions respectively of aniline hydrochloride and oxidised, with potassium dichromate. A mixture of the hydrochloride with two molecular proportions of metatoluylenediamine hydrochloride yields, on oxidation, a dye of the toluylene-blue class, but it was not found possible to obtain a colouring matter of the methylene-blue type from paradiamidodiphenylpiperazine. W. P. W.

Quinoline and Tetrahydroquinoline. By E. LELLMANN and H. REUSCH (*Ber.*, **22**, 1389—1392).—When tetrahydroquinoline is heated either with parachloronitrobenzene or orthobromonitrobenzene for two to three hours at 200°, a product is obtained consisting of a mixture of quinoline with unaltered tetrahydroquinoline and resinous matters. The oxidation of the tetrahydro-base to quinoline can readily be effected by boiling with nitrobenzene in a reflux apparatus for several hours.

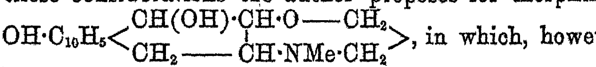
Orthocyanoquinoline, $C_9NH_6{\cdot}CN$, can be obtained in the pure state, free from the ana-isomeride (compare Fischer and Körner, Abstr., 1884, 1197) if an intimate mixture of sodium orthoquinolinesulphonate with five times its weight of potassium cyanide is distilled in a vacuum instead of at the ordinary pressure. It crystallises from alcohol in small, white needles, melts at 84°, yields a platinochloride, $(C_{10}H_6N_2)_2,H_2PtCl_6$, crystallising in orange-yellow needles, and is converted into quinolineorthocarboxylic acid by heating with concentrated hydrochloric acid at 150°. W. P. W.

Morphine. By L. KNORR (*Ber.*, **22**, 1113—1119; compare this vol., p. 417).—The oily base previously described (*loc. cit.*) as among the products of the decomposition of methylmorphimethine by means of acetic acid, is probably only impure methylmorphimethine which has escaped action. The second oily product mentioned was found to consist mainly of *β-hydroxyethyldimethylamine*,

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,$$

described by Ladenburg (Abstr., 1882, 166) under the name of dimethylalkine. The author has carefully examined this substance. It is best obtained by heating methylmorphimethine with acetic anhydride at 160—190° for 3—4 days. It boils at 128—130°. Its *acetyl-derivative* forms a crystalline *hydrochloride*, which again yields an *aurate*, $C_6H_{14}NO_2Cl,AuCl_3$, crystallising in scales. When the base is treated with methyl iodide, it is converted into choline.

From these and previous results the author concludes (1) that morphine is a tertiary base; (2) that morphine contains a methyl-group attached to nitrogen; (3) that methylmorphimethine contains two methyl-groups combined with nitrogen; (4) that morphine contains a partly reduced phenanthrene nucleus; (5) and that methylmorphimethine is decomposed by acetic anhydride into β-hydroxyethyldimethylamine and a phenanthrene-derivative; (6) that morphine contains a phenylic hydroxyl, an alcoholic hydroxyl, and an indifferent, probably etheric, oxygen-atom; (7) that the alcoholic hydroxyl of the morphine remains the same in methylmorphimethine, and only appears as a phenylic hydroxyl after decomposition of the latter base into acetomethyldioxyphenanthrene.

From these considerations the author proposes for morphine the formula  $OH{\cdot}C_{10}H_5{<}\begin{matrix} CH(OH){\cdot}CH{\cdot}O{-\!-}CH_2 \\ CH_2{-\!-}CH{\cdot}NMe{\cdot}CH_2 \end{matrix}{>}$, in which, however, it is doubtful whether the alcoholic hydroxyl is in the position assigned or is combined with the adjoining carbon-atom. L. T. T.

Meconarceïne and Narceïne Meconate. By E. MERCK (*Chem. Centr.*, 1889, 384, from *Pharm. Zeit.*, **34**, 90).—The meconarceïne obtained from France consists, according to the author's analyses, of a solution containing camphor, codeïne, and narceïne, the bases being in combination with an acid soluble in ether, but which the author could not identify. The meconarceïne obtained in Germany is a white powder consisting of a mixture of narceïne and meconic acid.

The author prepares narceïne meconate by mixing the acid and base in equimolecular proportions, which produces a lemon-yellow acid salt, soluble in hot water, little soluble in alcohol, readily soluble in 50 per cent. alcohol, and melting at 126°. Attempts to prepare the normal salt from narceïne (2 mols.) and meconic acid (1 mol.) resulted in the formation of products varying in composition, the first portions which crystallised out being richer in meconic acid than the last. J. W. L.

α-Hydroxycinchonine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **108**, 952—955; compare Abstr., 1888, 380, 508).—α-Hydroxycinchonine is obtained by the action of hot dilute sulphuric acid on cinchonine, and forms part of the bases which are insoluble in ether, but soluble in dilute alcohol. It is isolated by taking advantage of the comparative insolubility of the hydrochloride, which is readily purified by crystallisation from boiling water or dilute alcohol.

α-Hydroxycinchonine, $C_{19}H_{22}N_2O_2$, crystallises from alcohol in colourless flattened prisms, which melt at 252° with much decomposition. It is strongly dextrogyrate. In a 1 per cent. solution in alcohol of 97°, $[\alpha]_D = +182° 56'$ at 18°, in an aqueous solution containing 2 mols. HCl, $[\alpha]_D = +210° 76'$ at 19°. It is alkaline to litmus and phenolphthaleïn, and is insoluble in water, but dissolves readily in alcohol, acetone, benzene, and chloroform. The solutions of its salts are not fluorescent, and give with ammonia a precipitate which is soluble in excess. α-Hydroxycinchonine is isomeric with homoquinine, apoquinine, apoquinidine, and the hydroxycinchonine described by Schützenberger and Strecker.

α-Hydroxycinchonine forms basic salts which are feebly alkaline to litmus, and normal salts, which have an acid reaction. Almost all of them crystallise readily. The *basic hydrochloride*, $C_{19}H_{22}N_2O_2,HCl + H_2O$, forms long, colourless needles, which melt at 230° with decomposition and are almost insoluble in water and alcohol. The compound is dextrogyrate, and in a 1 per cent. solution containing 1 mol. HCl, $[\alpha]_D = +174° 37'$ at 13°. The *hydrobromide* has similar properties, crystallises with the same proportion of water, and melts at 232°. The *hydriodide* crystallises with 1 mol. H_2O in long needles, which melt with decomposition at 230°. The *platinochloride* is a yellow, amorphous substance, insoluble in boiling water; it contains 1 mol. H_2O, which is given off at 110°. The *aurochloride* is soluble in boiling water, from which it separates in yellow needles containing 1 mol. H_2O. Half the water is given off at 100°, and the remainder at 130°. The *basic oxalate* crystallises with 2 mols. H_2O in slender needles, which are only slightly soluble in cold water, and the *basic tartrate* also crystallises.

The methiodides and ethiodides are obtained by direct combination in presence of alcohol. The *methiodide* forms colourless, anhydrous nacreous lamellæ, melts at 241—240°, and is much more soluble than the corresponding cinchonine-derivative, dissolving readily in water and ethyl and methyl alcohols. The *dimethiodide* forms bulky, anhydrous, yellow, prisms, which melt with decomposition at about 241°; they are somewhat soluble in water, but dissolve only slightly in ordinary alcohol or concentrated methyl alcohol. The *ethiodide* crystallises with 1 mol. H_2O in long striated prisms, which become anhydrous at 150°, and melt with decomposition at 251°. It is less soluble in water than the methiodide, and dissolves but slightly in absolute alcohol. The *diethiodide* forms small, yellow, anhydrous prisms, melts with decomposition at 240°, and is more soluble in water than in alcohol. Ethyl bromide yields corresponding derivatives; the first forms colourless, anhydrous needles, which melt at 245°, and the second forms slender, colourless needles grouped in mamelons, very soluble in water and ordinary alcohol, but insoluble in ether and absolute alcohol.

If α-hydroxycinchonine is heated at 70—80° with two molecular proportions of acetic anhydride, it yields a diacetyl-derivative, a colourless resinous substance, which melts at 80—85°, and volatilises in a vacuum. It is insoluble in water, but soluble in alcohol, and forms salts which do not crystallise and are usually soluble. The platinochloride, $C_{19}H_{22}Ac_2N_2O_2,H_2PtCl_6 + H_2O$, is an amorphous chamois-coloured precipitate, which becomes crystalline in hot water and decomposes before melting.

The fact that α-hydroxycinchonine forms a diacetyl-derivative, whilst cinchonine forms only a monacetyl-derivative, supports the view that α-hydroxycinchonine is formed from cinchonine by assimilation of water and consequent introduction of another phenol function.

C. H. B.

New Compounds of the Cinchona Alkaloïds. By O. HESSE (*Chem. Centr.*, 1889, 519—520, from *Pharm. Zeit.*, **34**, 191—192).—*Quininephenol sulphate*, $C_{20}H_{24}N_2O_2,SO_3,C_6H_6O + 3H_2O$, is obtained by adding an equivalent quantity of phenol to a hot, aqueous solution of quinine disulphate. By heating the aqueous solution the normal sulphate crystallises out. Similarly the acid quinine sulphates of the higher phenols are changed into the normal salts by heating the aqueous solutions. In this manner the resorcinol, quinol, and pyrogallol normal salts have been prepared.

The phenol acid salts of hydroxyquinine, cinchonidine, and hydroxycinchonidine, behave in a similar manner.

The following normal sulphates have also been prepared:—

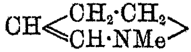
Quinineorcinol sulphate, $(C_{20}H_{24}N_2O_2)_2,SO_3,C_7H_8O_2 + 2H_2O$, colourless needles, little soluble in cold water; *quininecatechol sulphate*, $(C_{26}H_{24}N_2O_2)_2,SO_3,C_6H_6O_2 + 2H_2O$, colourless needles, the aqueous solution of which is coloured very dark green by ferric chloride; *cinchonidineresorcinol sulphate*, $(C_{19}H_{22}N_2O)_2,SO_3,C_6H_6O_2 + 5H_2O$, long colourless needles, easily soluble in water; *cinchonidinequinol sulphate*, $(C_{19}H_{22}N_2O)_2,SO_3,C_6H_6O_2 + 4\frac{1}{2}H_2O$, long needles, easily soluble in water. With ferric chloride the aqueous solution of the resorcinol compound is coloured violet, that of the quinol compound yellow, and that of the pyrogallol-derivative very dark blue. Excess of hydrochloric acid liberates the molecule of the phenol. No similar compounds were obtained from thymol and eugenol. J. W. L.

Hydrastine. By M. FREUND (*Ber.*, **22**, 1156—1160).—Acetic anhydride acts very energetically on hydrastineoxime (this vol., p. 627), with the formation of *diacetohydrastineoxime*, $C_{11}H_{12}N_2O_3Ac_2$. This substance crystallises in scales, soluble in boiling water and in hydrochloric acid, and melts at 121—122°. When heated with dilute soda, it dissolves and forms *monacetohydrastineoxime*, $C_{11}H_{13}N_2O_3Ac + 2H_2O$. This forms crystals which melt in their water of crystallisation at 90°, lose their water at 100°, and then re-melt at 139—140°. It is soluble in soda and hydrochloric acid.

The author has already (*loc. cit.*) described the formation of oxyhydrastinine by the action of potassium permanganate in the cold on hydrastine. He now finds that excess of the oxidising agent and slight heating carries the oxidation further to *hydrastinic acid*, $C_{11}H_{11}NO_5$, a substance which is soluble in alcohol and ether, almost insoluble in chloroform. It crystallises in flat needles and melts at 164°. It gives no precipitate with silver or lead salts. The *barium salt*, $(C_{11}H_{10}NO_5)_2Ba + 5H_2O$, forms white needles, soluble in water, very sparingly so in alcohol. It loses its water of crystallisation at 130°. When the free acid is melted it gives off carbonic anhydride, and yields a crystalline substance melting at 215°, and soluble in soda. A small quantity of a substance melting at 260° is also formed. When boiled with dilute nitric acid, the acid yields a crystalline compound melting at 230°. L. T. T.

Constitution of Ecgonine. By C. STOEHR (*Ber.*, **22**, 1126—1129).—By the distillation of ecgonine with a mixture of zinc-dust and lime, the author obtained methylamine, α-ethylpyridine, and small quantities of a neutral oxy-compound, seemingly resembling tropilen, and of a hydrocarbon. The two latter are being investigated. These results support the theory that ecgonine is a hydrogenised pyridine-derivative. L. T. T.

Conversion of Anhydroecgonine into Pyridine. By A. Einhorn (*Ber.*, **22**, 1362—1368; compare this vol., p. 628).—The solution obtained by heating anhydroecgonine with concentrated hydrochloric acid, contains methyl chloride, hydrocarbons, ammonia, methylamine, and other basic compounds. After removing the neutral compounds by distilling with steam, the solution is mixed with alkali, again distilled with steam, and the distillate (A) shaken with ether. The ethereal extract contains a secondary and a tertiary base, which can be separated by means of nitrous acid. The nitroso-compound is decomposed by boiling concentrated hydrochloric acid, yielding a secondary base, the *aurochloride* of which crystallises from hot water or alcohol in needles, melts at 186—187° with decomposition, and gives a pyridine base when distilled over zinc-dust.

The *aurochloride*, $C_7NH_{13},HAuCl_4$, of the tertiary base, crystallises in small needles, melts at 212°, and is rather sparingly soluble in water. The *picrate*, $C_7NH_{13},C_6H_3N_3O_7$, crystallises from hot water, in which it is very sparingly soluble, in long needles. The *hydrochloride* is very hygroscopic. The free *base* is an oil, soluble in water, and has probably the constitution  $CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH\cdot NMe\end{matrix}{>}CHMe$. When heated at 280° with concentrated hydrochloric acid, it is decomposed into hydrocarbons, methyl chloride, and a mixture of bases, one of which forms a nitroso-compound. If this basic mixture is treated with hydrochloric acid, the solution evaporated to dryness, and the residue distilled over zinc-dust, a pyridine base, possibly picoline, is obtained.

When the bases obtained by heating anhydroecgonine with hydrochloric acid are directly converted into the hydrochlorides, and the latter distilled over zinc-dust, hydrocarbons, pyridine, and another oily base are formed. The pyridine can be isolated by means of the aurochloride; this salt, and the platinochloride, were found to be identical in all respects with the corresponding compounds prepared from ordinary pyridine.

The aqueous solution (A) which remains after extracting the secondary and tertiary base with ether, contains two other bases, which can be separated by fractionally recrystallising their aurochlorides from alcohol. The one gives a sparingly soluble aurochloride which crystallises in long, slender needles melting at 247—248°. The other, the principal portion of the mixture, forms a readily soluble aurochloride, which separates from hot water in crystals melting at 207·5°; when distilled over zinc-dust, it yields pyridine.

These experiments prove that cocaïne is a pyridine-derivative, so that its constitution may be considered as settled. F. S. K.

Chemistry of Gluten. By A. Krüger (*Chem. Centr.*, 1889, 433—434, from *Rostocker Zeit.*, 1889, No. 105).—The barium compound of gluten was obtained by adding an excess of baryta-water to the solution of gluten, and then precipitating the excess of barium hydroxide with carbonic anhydride, and finally concentrating the filtrate. The salt was not obtained in the pure state, foreign mineral matter always remaining with the gluten.

β-Gluten, obtained from impure commercial gluten by heating it with water at 100° under pressure, combined with more barium than α-gluten. Neither could, however, be obtained free from foreign matter. The specific rotatory power changes from —167·5° to —136° with the change of α-gluten into β-gluten. J. W. L.

Products of the Action of Superheated Steam on Fibrin. By R. Neumeister (*Zeit. Biol.*, **26**, 57—83).—The albumoses are formed from proteïds, either by heating them with dilute mineral acids, or by the action of ferments like pepsin and trypsin. In the present research the products of the action of steam on fibrin were investigated. The experiments were conducted in sealed tubes raised to the temperature of 150—160°. There was an abundant production of hydrogen sulphide. In an hour's time, the fibrin was dissolved; the solution was opalescent, and there was no coagulation on boiling it. On saturating it with sodium chloride, a precipitate was obtained; this was filtered off, and on making the filtrate strongly acid, another precipitate was obtained. These two precipitates did not consist of ordinary albumoses, but of substances to which the names atmid-albumin and atmid-albumose are respectively given. Each was obtained pure by dissolving it in ammonia, neutralising with hydrochloric acid, and removing the salt by dialysis. Ammonia was used, as ammonium chloride was found to be more easily removable by dialysis than sodium chloride. The solution was then concentrated, the proteïd precipitated by alcohol, washed with alcohol and ether, and finally dried. Smaller quantities of the same substances were obtained by simply boiling fibrin or white of egg for several hours with water. After separation of the atmid products small quantities of peptone remained in solution.

Atmid-albumin is soluble in distilled water; on boiling there is no coagulation, or only an opalescence of the solution if concentrated. It is precipitated by nitric acid; on heating this does not disappear, but dissolves in the hot liquid on the addition of more nitric acid. This clear solution does not become cloudy on cooling. On adding still more nitric acid there is a further precipitate, which like an albumose dissolves on heating, and reappears on cooling. It is precipitated from neutral solutions almost completely by saturation with sodium chloride; in a faintly acid solution it is completely precipitated by this salt. Saturation with ammonium sulphate causes complete precipitation independently of the reaction. It is further characterised by being precipitated by dilute acetic, hydrochloric, and other acids; the precipitate is soluble in excess of the reagent. With copper sulphate and sodium hydroxide, it gives the violet colour that albumin shows. Millon's reagent gives only a faint coloration. Lead salts and sodium hydroxide give no black coloration. Atmid-albumin is soluble in urine, and a proteïd with similar properties was described in a case of morbid urine by Thormählen (*Virchow's Archiv*, **108**, 322). Atmid-albumin is probably the same substance as that described by Krukenberg in a similar investigation as anti-albuminoïd (*Sitz. Jena Gesell. Med. Naturwiss.*, 1886).

Atmid-albumose is only precipitable by sodium chloride in a strongly acid solution. It is also completely precipitable by saturation with ammonium sulphate. It is precipitable by nitric acid like the primary albumoses; it is precipitated by copper sulphate, but soluble in excess. It gives the biuret reaction; it gives a well-marked colour with Millon's reagent. Like its mother substance atmid-albumin, it is precipitated by dilute acids, the precipitate being soluble in excess. Elementary analysis gave the following results:—

	C.	H.	N.	S.	O.
Atmid-albumin....	48·58	7·62	14·43	0·39	28·98
Atmid-albumose ..	48·40	7·55	13·58	0·37	30 10

Both substances resisted very strongly the action of the digestive juices; but by means of dilute sulphuric acid, deutero-albumose and peptone were obtained from each. As one would expect from their behaviour to pepsin, both substances, when injected into the circulation of the dog, were excreted in the urine in an unchanged condition.

W. D. H.

Physiological Chemistry.

Change of Substance in the Horse at Rest and at Work. By N. ZUNTZ, C. LEHMANN, and O. HAGEMANN (*Bied. Centr.*, **18**, 293—296).—Respiration experiments were made with horses at rest and in motion, the expired gases being collected by means of a brass mask over the horse's mouth, and examined. In some cases tracheotomy was performed, and the gases obtained directly from the trachea. The apparatus used for making the horse do the desired amount of work was a specially constructed treadmill. This and the other apparatus used are fully described with sketches in the original paper (*Landw. Jahrb.*, **18**, 1—156). In some experiments the expired air contained more oxygen and less carbonic anhydride when the horse was working than when at rest; in other cases the reverse was observed. During the period directly following work the rate of respiration remained still much above the normal rate, but there was no increased oxidation, the oxidation becoming normal the moment the work ceases. Hence the amount of oxygen in the expired air is high, and that of carbonic anhydride very small during this period. The oxygen deficit is, however, more diminished than the amount of carbonic anhydride; this is due to the fact that the lessened pressure of carbonic anhydride in the lungs gives rise to an increased evolution from the blood. In this way the whole body becomes poorer in carbonic anhydride.

Determinations of oxygen consumed and carbonic anhydride produced by horses at rest and working gave different results with different kinds of work; in nearly all cases in which two periods of work follow one another, the second period gave rise to a less consumption of oxygen, and less production of carbonic anhydride, so that the production of work takes place with greater economy after a period of activity.

There is no constant relation between the consumption of substance and amount of work; the whole organisation of an animal, its individual and periodically different behaviour, variety of feeding, &c., make great differences in the economical use of its strength, even in doing the same work. N. H. M.

Digestion of Elastic Fibres and Allied Structures. By A. Ewald (*Zeit. Biol.*, **26**, 1—56).—Elastic fibres from the *ligamentum nuchæ* of the ox were subjected to tryptic digestion. The digestive fluid (prepared according to Kühne's method) completely dissolved fibrin in 3—5 minutes. In the experiments, putrefaction was prevented by means of thymol. The pieces of ligament were placed in small test-tubes, the digestive fluid added, and microscopical examinations were made of the elastic fibres at intervals. At 40° no change took place until one hour and a-half had elapsed; then in the thickest fibres cross markings were visible in the central parts; these were really small vacuoles. They increased in number and size, until in six hours a central canal was hollowed out along the fibre; and after 24 hours the entire fibre was dissolved. The smaller fibres, in which the more difficultly digestible outer shell is present in proportionally greater amount, were digested somewhat more slowly. At the ordinary atmospheric temperature digestion also took place, but much more slowly. If instead of the fresh fibres, pieces of the ligament were used which had been previously boiled, or treated with 0·2 per cent. hydrochloric acid, or with alcohol, it was found that they were much more easily digestible. In peptic digestion the most marked difference found between it and tryptic digestion was an intermediate swollen condition of the fibres, which occurred before they were dissolved. This swollen material is, however, not collagenous, as Pfeuffer (*Arch. mikr. Anat.*, **16**, 17) has considered. Putrefaction was found to produce the same cross markings in the elastic fibres as tryptic digestion. From these experiments, the conclusion is drawn that an elastic fibre consists of two substances; both are digestible by trypsin and by pepsin at 40°; one is strongly refracting, and dissolves easily in cold acid solutions of pepsin; the other is not dissolved, but only swollen in the cold by acid solutions of pepsin. If the fibres are just subjected to tryptic digestion for a short time, peptic digestion in the cold then produces a simple solution without preliminary swelling.

Pieces of elastic ligament were placed in various reagents, and the effect of digestive fluids on such fragments was then investigated.

0·5 per cent. osmic acid coloured the fibres a yellowish-brown, but otherwise produced no change in them visible with the microscope. Tryptic digestion produced much more rapid solution of these than of the fresh fibres; but they were quite insoluble in peptic fluids. After treatment with pepsin solutions, however, they were found to be as digestible as fibrin in trypsin solutions. Stronger solutions of osmic acid (2 per cent.) first cause a swelling of the fibres to three or four times their original bulk; in these conditions they were seen to be made up of concentric laminæ of alternately darkly and lightly stained substance. Later, they were entirely dissolved.

Müller's fluid and chromic acid ($\frac{1}{30}$ per cent.) in the dark, were found to produce no great difference in the digestibility of the elastic fibres, either with regard to pepsin or trypsin; but the same strength of chromic acid solution in the light rendered the tissue quite indigestible in solutions of trypsin, although in solutions of pepsin it was still digestible. A concentrated solution of picric acid was found to produce little or no effect on the digestibility of the tissue.

A similar series of observations was made on the sarcolemma of muscle fibres, on the basement membrane of the gastric glands, and on ordinary connective tissue fibres. The chief comparative results are collected together in the following table:—

Treatment before tryptic digestion.	Effect of tryptic digestion on			
	Elastic fibres.	Sarcolemma.	Basement membrane.	White connection tissue fibres.
Without treatment	Digested	First swollen, then digested	Same as sarcolemma, only more slowly	Not digested.
Boiled	Digested	—	Digested without preliminary swelling	Digested.
Alcohol	Digested	First swollen, then digested	Same as sarcolemma, only more slowly	Not digested.
Alcohol, then boiled	Digested	Digested without preliminary swelling	Digested	Digested.
Osmic acid, 0·5 per cent.	More easily digested	Not digested	Not digested	Not digested.
Osmic acid, 0·5 per cent., then boiled	More easily digested	Not digested	Not digested	Digested.

W. D. H.

Composition and Digestibility of some Foods, with Observations on the Determination of Digestibility of Proteïn and Carbohydrates. By W. A. JORDAN, J. M. BARTLETT, and L. H.

MERRILL (*Bied. Centr.*, 1889, 296—308, from *Agricultural Science*, **2**, 283—302).—The digestibility of foods was determined by experiments with sheep, and also by digesting the finely-ground substance with pepsin and pancreas juice at 40° for 24 hours. The latter method gave, with some exceptions, higher coefficients for albumin than the experiments with animals, which is partly due to the whole nitrogen of the excrement being taken as indigestible albumin. It is therefore necessary to determine, if possible, how much of the nitrogen of the excrement was contained in the really indigestible portion of the food, and how much is present as bile constituents, &c. The methods employed were: (1) Successive treatment of the fæces with ether, alcohol, and hot water; (2) the same treatment, followed by extraction with cold lime-water; (3) digestion with gastric juice. The nitrogen in the residue was then determined. The results obtained by four methods are given. (A) experiments with animals; (B) the same corrected by treatment of the fæces by method (2) above; (C) the same corrected by treating the fæces with gastric juice; (D) artificial digestion of the food with gastric juice and pancreas extract. The results vary very much, but the method B seems to be the most satisfactory; by method C too much nitrogen may be extracted.

The non-nitrogenous constituents of food, the readily digested carbohydrates, on the one hand, and the substances difficult to digest on the other, were determined in several foods, and also in the fæces of animals fed with known amounts of the foods. From the results so obtained the amount of sugar and starch, and of non-nitrogenous constituents (not sugar and starch) digested, are calculated.

N. H. M.

Amount of Urea in Blood and Muscle. By GRÉHANT and QUINQUAUD (*Compt. rend.*, **108**, 1092—1093).—50 grams of chopped rabbit muscle was allowed to remain in contact with alcohol overnight and the latter was then squeezed out and evaporated on a water-bath. The residue was dissolved in water, placed in the receiver of a mercury pump, and treated with hypobromite. The results obtained are expressed in milligrams of urea per 100 grams of substance:—

	1.	2.
Blood	35·1	98·2
Muscle	37·8	107·2

Most probably the formation of urea takes place in the muscles. The differences are still greater if allowance is made for the fact that the proportion of solid residue in muscle (22·1 per cent.) is greater than in blood (17·3 per cent.).

The muscle of the ray contains 50 times as much urea as the muscle of the rabbit.

C. H. B.

Composition of Milk produced on English Dairy Farms. By P. VIETH (*Jour. Roy. Agr. Soc.* [2], **25**, 180—202).—The paper contains the results of analyses of 84,746 samples of milk made from 1881—1888. The milk supplied to London comes from at least half the English counties, and is therefore fairly representative. The determinations were: Total solids, non-fatty solids (important as being the most constant factor), and fat, which is the most valuable constituent. The non-fatty solids contain, with little variation, six-twelfth parts of milk-sugar, one-twelfth part ash, and five-twelfths proteïds, rather more than two-thirds of the latter being caseïn, The results are shown in curves, the most striking features of which are the great uniformity of the non-fatty solids and the rather large variations in the percentages of fat which cause the total solids to fluctuate to about the same extent. The best milk is obtained in November, when most cows give a limited amount; in the spring months there is an increased flow of milk of a poorer quality. The composition of morning and evening milk is also shown in diagrams: the evening milk is almost invariably the richer, and this difference is ascribed to the inequality of the intervals between the two milkings.

Notwithstanding the variations in the milk, the sp. gr. of the mixed yield of several cows rarely falls outside the limits of 1·030 and 1·034, and this is explained by the fact that the higher percentage of fat, which tends to lower the sp. gr., is generally accompanied by an increased amount of non-fatty solids exercising an influence in the opposite direction. Even in the case of milk of individual cows there are comparatively few exceptions, and of these by far the greater number are not lower than 1·029 nor higher than 1·035. The lowest and highest figures observed were 1·0240 and 1·0365 respectively.

N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation of the Juice of the Sugar-cane. By V. Marcano (*Compt. rend.*, **108**, 955—957).—When the juice of the sugar-cane is allowed to ferment spontaneously in tropical climates, the ferment which develops consists of very brilliant, rounded cellules impregnated with granules. They are smaller than beer yeast and are isolated instead of being arranged in chains and bunches. This ferment retains its individuality, even after several cultivations, so long as it remains in the same medium. In liquids very rich in sugar, or in solutions containing starch or dextrin, it changes into a mycelium, the filaments of which invade the whole liquid. If, however, the mycelium is put back into the ordinary juice of the sugar-cane, it returns to the original form. In all industrial fermentations, and especially in those which take place slowly or in presence of an excessive supply of air, simultaneous presence of yeast and mycelium is observed.

The ferment shows a maximum activity at 30—35°, and is very sensitive to a reduction of temperature. Even at 18—20° fermentation is much slower, there is a tendency to acidify, and the yield of alcohol is but moderate. The best yield of alcohol is obtained with liquids containing 18 to 19 per cent. of sugar, which is the mean amount present in the juice of the cane. The ferment secretes a diastase which inverts the saccharose. When the liquid is distilled, a gas with a diagreeable odour is evolved and the first fraction consists of impure methyl alcohol. This is followed by ethyl alcohol of a high degree of purity. The last fractions contain no higher alcohols, but have a disagreeable flavour owing to the presence of an oily acid which is insoluble in water and with alkalis forms salts which are insoluble in dilute alcohol. It can be separated by taking advantage of this property.

The yield of alcohol by spontaneous fermentation is inferior to that obtained with beer yeast. Neither glycerol nor succinic acid is formed, but the liquid always contains mannitol equal to about 1·4 per cent. of the sugar decomposed. C. H. B.

Alcoholic Fermentation of Milk. By Martinand (*Compt rend.*, **108**, 1067—1069).—Under suitable conditions alcoholic fermentation of the sugar and coagulation of the milk take place with all kinds of yeast, including that described by Duclaux (*Ann. Institut Pasteur*, December, 1887). If a 10 per cent. solution of glucose or maltose is mixed with 10 to 80 per cent. of milk, and Duclaux's yeast or *Saccharomyces cerevisiæ*, *ellipsoideus*, *pastorianus*, or *apiculatus* is added, the milk coagulates in from 17 to 60 hours. The same result is obtained with saccharose, except with *S. apiculatus*, a result due to the absence of invertin in *S. apiculatus*. Coagulation is not due to the formation of an acid, since a solution of the fermented sugar cannot coagulate milk after filtration through a Chamberland's filter.

With Duclaux's yeast, the time required for the coagulation of milk varies with the quantity of added water. Pure milk, or milk with less than 20 per cent. of added water, does not coagulate, but in other cases coagulation takes place after a time which is shorter the greater the proportion of water. With 80 and 90 per cent. of water, however, coagulation does not take place. The quantity of alcohol produced decreases as the proportion of water increases. If the diluted milk is mixed with 10 per cent. of fermentable sugar, coagulation takes place in all cases, the time required being longer the greater the proportion of water.

When milk is filtered through a Chamberland's filter, it becomes turbid before any appreciable quantity of alcohol is formed. With the same milk not filtered, coagulation is not sudden, but a precipitate of caseïn forms and increases until fermentation ceases. Precipitated caseïn, dissolved in a solution of sugar and filtered through Chamberland's filter, shows the same phenomena when fermented. The fact that the action on soluble caseïn, suspended caseïn, and precipitated caseïn is the same, is readily explained by assuming that in milk there is only one albuminoïd. C. H. B.

Composition of Vegetable Cell-membrane. By E. Schulze (*Ber.*, 22, 1192—1196; compare Reiss, this vol., p. 687).—It has been previously shown (compare Schulze and Steiger, Abstr., 1887, 460) that the seeds of the yellow lupine contain an insoluble carbohydrate (paragalactin) which, when boiled with dilute sulphuric acid, is converted into galactose. This carbohydrate occurs in the thickened walls of the cells of the cotyledons, and serves as a reserve material which is used up in the germination of the seed.

Carbohydrates, insoluble in water, which resemble paragalactin in this, that they are readily converted into saccharoses by dilute mineral acids and into mucic acid by nitric acid, are widely diffused in the vegetable kingdom. They occur generally in the seeds, for example, in the soja-bean, peas, vetches, field-beans, coffee berries, date stones, young red clover, lucerne, and in the hard parts of the cocoa and palm nut. The carbohydrates can be isolated by extracting the finely-divided seeds with ether, treating the residue first with cold dilute potash and then with water, and if starch is present removing it with extract of malt. The residue is boiled for an hour with 5 per cent. sulphuric acid, the solution separated from insoluble substances, diluted, boiled again for some hours and freed from sulphuric acid by means of barium carbonate. The filtrate is evaporated, the residue extracted with warm alcohol and the alcohol slowly evaporated. All the sugar solutions obtained in this way yielded, on oxidation with nitric acid, mucic acid in larger or smaller quantities, so that galactose was present in every case. In two cases (coffee berries and soja-beans) the sugar which first separated from the alcoholic solution was isolated and obtained in a pure condition; its rotatory power was identical with that of galactose, but many, if not all, the solutions most probably contained seminose (compare Reiss, *loc. cit.*) as well as other saccharoses. In several seeds the authors found carbohydrates which, on hydrolysis, gave arabinose and similar compounds.

That the insoluble carbohydrates referred to above are really constituents of the cell-wall was proved by microscopic observations. The thickened cell-walls of the cotyledons of the date, cocoa-nut, palm-nut, coffee berry, and seeds of leguminosæ, from which the fat and albuminoïds have been removed as described above, resist the action of ammoniacal copper oxide solution, and only give a slight coloration with iodine and zinc chloride; but if the carbohydrates have been removed by heating with dilute acids, the residual portions of the cell-wall generally dissolve easily in the ammoniacal solution and give a distinct coloration with iodine and zinc chloride.

These results show that the cell-membrane of the seeds investigated contains several carbohydrates, as well as the substance which is called cellulose; the former differ from the latter in being insoluble in ammoniacal copper oxide solutions and in being far more readily converted into saccharoses, other than dextrose, by acids.

F. S. K.

Note.—According to Fischer and Hirschberger (this vol., p. 687) seminose is identical with mannose. A. J. G.

Physiology of Tannin. By G. KRAUS (*Bied. Centr.*, **18**, 330—334).—The formation of tannin in leaves depends on the presence of light and carbonic anhydride: the outer leaves of a plant exposed to direct sunlight will contain far more tannin than the inner leaves.

Leaves which are not green are not capable of producing tannin. It must not, however, be assumed that tannin is a product of assimilation of the chlorophyll-grains, inasmuch as there are innumerable plants which assimilate carbonic anhydride without ever producing tannin; and oak, willow, and alder leaves assimilate in dull weather without the amount of tannin being increased. The tannin produced in the leaves passes into the branches and roots, and there is no experimental evidence to show that the tannin which has once passed into the rhizome undergoes further change; there is rather an increase in the amount of tannin in the rhizome through a production in the dark.

With regard to the use of tannin to leaves, the author is inclined to view it as a protecting agent either to prevent the plant from being eaten or to prevent rotting, &c.

Falling leaves contain as much tannin as they did during their best time of growth, indicating that the leaf tannin is of no value to the plant.

During germination in the dark of seeds containing tannin (such as the seeds of oak and horse-chestnuts) there is no diminution, but an increase in the amount of tannin.

There is not yet sufficient evidence to show whether tannin is produced from non-nitrogenous substances, or whether it is formed in the conversion of nitrogenous compounds into albuminoids. It seems probable that aromatic compounds may be formed in the production of albumin, some of which are used in the building up of albumin molecules, whilst others yield tannin. N. H. M.

Cane-sugar from Maize. By J. H. WASHBURN and B. TOLLENS (*Ber.*, **22**, 1047—1048).—The authors have succeeded in isolating crystalline cane-sugar from ripe maize, and also, but in rather larger quantities, from ripe American sweet-maize. F. S. K.

A Volatile Base from the Root of Cephaëlis Ipecacuanha. By E. M. ARNDT (*Chem. Centr.*, 1889, 433, from *Zeit. österr. Apoth. Vereins*, **27**, 129).—By distilling the pulverised root with sodium carbonate, a little ferric chloride and water, an alkaline distillate is obtained, while a white crystalline substance is deposited in the condenser. The distillate is yellow, fluorescent, and smells of ammonia. When evaporated with hydrochloric acid, and the residue heated with strong sodium hydroxide solution, a volatile substance, having the smell of trimethylamine, is obtained. If the residue is heated with barium hydroxide instead of sodium hydroxide, the distillate has no smell of trimethylamine. It is alkaline, and leaves a crystalline, fluorescent residue when evaporated spontaneously. The hydrochloride of the new base crystallises in octahedrons, which fluoresce. The nitrate does not crystallise. The platinochloride is yellow; the potassio-mercuric iodide is white; Nessler's reagent produces a yellowish-red precipitate, and iodine solution an amorphous, brown precipitate. J. W. L.

Colouring Matters of Fungi. By W. ZOPF (*Chem. Centr.*, 1889, 291—293, from *Bot. Zeit.*, 1889, 53—61, 69—81, 85—92).—The fungus, *Polyporus hispidus*, contains a beautiful yellow, resinous substance which much resembles the gamboge of *Garcinia morella* in many of its reactions, and the author names it therefore fungus-gamboge. Another, a yellow or greenish-yellow substance, occurs in the same fungus, and also has an acid character.

In the hymenium of the *telephoria*, a colouring material, composed of at least three different substances, is found. It includes *telephoric acid*, a beautiful red dye, a yellow non-crystalline substance, and a yellow resin acid. The polyporus, *Trametes cinnabarina*, contains two beautiful yellow substances, the one forming cinnabar-coloured crystals, the other being probably a resin. These substances all occur in the hymenium.

The author has found a lipochrome in *Bacterium egregium*, an orange-yellow, fatty substance. The alcoholic solution shows an absorption band at F, and a weaker one between F and G in the spectrum, corresponding with those of the spectra of anthoxanthine and the fatty colouring material of the *uridineæ*. The formation of the lipochrome occurs independently of the presence or absence of light.

J. W. L.

Gluten in Wheat. By A. GATELLIER and L. L'HOTE (*Compt. rend.*, **108**, 1018—1019 and 1064—1066).—Three samples of wheat from different localities were examined, with the following results:—

	Nitrogen.	Gluten.
American	2·31	14·44
Ferté-sous-Jouarre..........	1·98	12·37
Vitry-le-François...........	1·96	12·25

Two different species of wheat were grown at Luzancy under precisely the same conditions of soil, previous crop, manure, &c.; the species Victoria gave 2·01 of nitrogen or 12·56 of gluten, and the species Bordeaux 1·94 of nitrogen or 12·12 of gluten.

A large number of species was grown near Meaux, after a crop of beet which had been treated with farmyard manure and sewage, the wheat itself being manured with 400 kilos. of phosphatic guano per hectare:—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Nitrogen	1·53	2·27	1·82	1·82	1·64	1·82
Gluten	9·56	14·18	11·37	11·37	10·25	11·37

	(7.)	(8.)	(9.)	(10.)	(11.)	(12.)
Nitrogen	1·70	1·76	1·82	1·65	1·77	1·92
Gluten	10·62	11·00	11·37	10·31	11·06	12·00

(1) Bearded Australian, (2) March wheat of Brie, (3) Red Scotch, (4) Dattel, (5) Guimel, (6) White Chiddam, (7) Belotour ka, (8) Bergues, (9) White Victoria, (10) de Noë, (11) Roseau, (12) de Crépy.

The extreme variations are from 9·56 to 12·00 per cent. of gluten; the March wheat of Brie may be regarded as abnormal. There is no relation between the weight of the crop and the richness of the grain in gluten, just as there is no relation between the weight of beet crops and the proportion of sugar which they contain.

45 varieties of wheat obtained by crossing, grown under similar conditions in 1887, gave as a maximum percentage of gluten 19·18, and as a minimum 14·31. In 17 varieties grown at Capelle, F. Desprez found a maximum of 13·6 per cent. of gluten and a minimum of 9·39.

Four varieties grown on two different soils gave the following results:—

	Red.	White Victoria.	Bergues.	Shireff.
At Ferté-sous-Jouarre	17·31	17·68	16·18	16·12
At Capelle..........	13·61	12·58	13·10	9·89
Difference....	3·70	5·10	3 08	6·23

Three other varieties grown at Ferté-sous-Jouarre, in a soil containing phosphoric anhydride 3·050 grams, and nitrogen 2·230 grams per kilo., and at Luzancy, in a soil which contained 1·030 grams of phosphoric anhydride and 1·520 grams of nitrogen per kilo., gave the following results:—

	Shireff-Hungary.	Hungary Shireff.	Belotourka Shireff.
At Ferté-sous-Jouarre ...	15·75	15·43	15·31
At Luzancy	13·18	11·87	12 81
Difference........	2·57	3·56	2·50

It follows that different varieties grown in the same soil, and the same variety in different soils, may contain very different amounts of gluten. English wheat as a rule is poor in gluten, whilst that grown on rich nitrogenous earths in America and Australia is rich in gluten. The latter wheat forms grains which are elongated instead of rounded. A large yield of wheat containing a high percentage of gluten is secured by selecting good seed and growing it in soil which contains a sufficient but not excessive supply of nitrogen.

C. H. B.

The History of a Field newly laid down to Permanent Grass. By Sir J. B. Lawes (*Jour. Roy. Agric. Soc.* [2], **25**, 1—24). —The soil of the field is a heavy loam with reddish-yellow clay subsoil and chalk below. The field had been under arable culture until 1856. After the first few years, the plan adopted for manuring was to apply London dung every other year, occasionally every third year, and artificial manures (superphosphate, potassium sulphate, and sodium nitrate) every year, with one or two exceptions. The former was to maintain the character of the herbage; the latter to secure a good yield of hay. With regard to sodium nitrate, the best results were obtained by using two-thirds cwt. per acre; a larger amount gave a too stemmy and almost exclusively grassy herbage. By judicious manuring the yield of hay has been considerably increased, and at the same time there has been a gradual improvement in the condition of the land. With regard to the constituents supplied in the manures and removed in the crops, considerably more nitrogen and phosphoric acid were supplied than were removed in the crops, but the amounts of potash supplied and removed were about the same. The average amounts removed per acre are: nitrogen, 58·2 lbs.; phosphoric acid, 15·5 lbs.; and potash, 62·1 lbs. The exhaustion of potash is thus very great, and it is important that it should be made up again. The loss of phosphoric acid and potash by drainage is not appreciable, and although nitrogen applied as nitrates or ammonium salts, and even in organic matter to arable land, may suffer considerable loss in wet seasons, and when no crop is growing, it is probable that the loss of nitrogen will be much less in the case of mixed grass land. An excess of dung applied to arable land or to water-logged soil may lose through evolution of free nitrogen.

Changes within the Soil in the Formation of the Meadow.—Arable land after the removal of a grain crop contains a very small amount of roots; in the case of barley, four soil samples showed an average of 536 lbs. per acre in the surface soil 9 inches deep. Of above ground residue, or stubble, there was 1104 lbs. per acre. The nitrogen in the stubble and roots together amounted to about 8½ lbs. per acre. In the same field, but with clover, there was a much greater amount of above and underground residue, and the two together contained over 90 lbs. of nitrogen per acre. In old grass land, the average amount was 16601 lbs. of vegetable matter, containing about 125 lbs. of nitrogen per acre in the 9 inches of surface soil. With regard to the soils themselves, the soil of the barley land (9 inches deep) weighed 2600000 lbs. per acre, excluding roots, stones, and moisture, and contained 3682 lbs. of nitrogen (= 0·1416 per cent.). The dry clover land soil contained 4072 lbs. of nitrogen (= 0·1566 per cent.) The same bulk of grass land soil weighed only about 2000000 lbs.; it contained 0·2346 per cent. of nitrogen, so that the total nitrogen amounted to 4692 lbs. per acre. With the increase of nitrogen in the conversion of arable into grass land, there is also a considerable increase in the amount of carbon. Whilst the Rothamsted arable land contains only 10 or 11 parts of carbon to 1 of nitrogen, the soil of the grass plots contains about 13 or 14 parts of carbon to 1 of nitrogen.

The following table shows the constituents in lbs. per acre in the first 9 inches of the soil of the meadow in 1879 and in 1888. In 1879 the numbers are the mean of those furnished by six samples, and in 1888 by five samples from different parts of the field :—

	Original soil.	Stones, &c.	Roots, &c.	Water.	Fine, dry soil.	Nitrogen.	
						lbs.	per cent.
1879..	3697609	907618	11561	769846	2008584	4097	0·2041
1888..	3366915	904387	10400	543150	1908978	4604	4·2414

In 1888 there was about 330000 lbs. less of original soil per acre, and nearly 100000 lbs. less dry soil (corresponding with about 5 per cent.) than in 1879. As regards the nitrogen there has been a gain of 507 lbs. per acre in the nearly 10 years. No samples were taken from the field before 1879, but from many results obtained from other fields, it may be assumed that at the commencement (1856) the surface soil (9 inches) would contain about 0·14 per cent. of nitrogen. But the weight of fine dry soil to the depth of 9 inches would, when arable, be about 2400000 lbs. per acre instead of about 2000000 lbs. as at present. It is thus necessary to deduct 400000 lbs. (one-sixth of original weight), and to deduct the amount of nitrogen it would contain from the total, and calculate the percentage in the remaining upper 2000000 lbs. Taking the original 2400000 lbs. at 0·14 per cent. of nitrogen, the total amount to the depth of 9 inches would be 3360 lbs. per acre. Assuming the lower 1½ inch (or one-sixth) to contain only 0·08 per cent., the amount of nitrogen to be deducted would be 320 lbs., so that the upper 2000000 lbs. of the fine, dry soil would contain 3040 lbs. of nitrogen (= 0·152 per cent.) in 1856. Having got an estimated percentage and total amount of nitrogen in 2000000 lbs. of soil in 1856, and actual determinations in the same amount of soil in 1879, it is necessary to correct the results obtained in 1888 (when the same bulk of surface soil weighed little more than 1900000 lbs.) in order to be able to compare the amounts of nitrogen at different dates. Assuming that 100000 lbs. deficiency of weight in 1888 being subsoil would contain about 0·09 per cent. of nitrogen, the calculation is as follows:—91000 lbs. of subsoil contains 82 lbs. of nitrogen, which added to 4604 (the amount by actual determinations in 1908978 lbs.) gives 4686 lbs. in 2000000 lbs. of soil corresponding with 0·231 per cent. These results show that there was an average yearly gain (independently of the visible and separated vegetable matter) of 45·7 lbs. per acre from 1856 to 1879, and of 59·9 lbs. over the last 10 years. The average gain over the last 23 years has been nearly 52 lbs. per acre. Of this amount a portion is due to excess of nitrogen supplied in manure over the amount removed by the crop; other sources of nitrogen are the cake or corn given to cattle feeding off the second crops (reckoned at 5 lbs. per acre), and the combined nitrogen in rain, &c. (reckoned at 5 to 10 lbs. per acre).

There is, however, still a certain amount of gain not accounted for, the source of which must be either in the subsoil, or the air, or both. There is much experimental evidence indicating that some leguminous plants derive a considerable quantity of nitrogen from the subsoil, and there seems no reason to doubt that the deep-rooting plants of the mixed herbage of grass land, whether leguminous or otherwise, may also avail themselves of subsoil nitrogen. The nitrogen so gained from the subsoil will be left in the surface soil. It is, indeed, very probable that the greater part, if not all, the nitrogen in question is due to nitrogen of the subsoil. That agricultural plants do not themselves directly assimilate free nitrogen by their leaves may be safely concluded from the results of experiments of Boussingault and of those made at Rothamsted. On the other hand, Hellriegel and

Wilfarth's experiments (this vol., p. 640) indicate that the free nitrogen of the air is assimilated by some leguminous plants under the influence of micro-organisms in the soil; and experiments with peas recently made at Rothamsted also seem to indicate a gain of nitrogen beyond that supplied in a combined form. Should it be finally established that such an action does take place, it is obvious that part at any rate of the gain of nitrogen by the soil of grass land may be due to the free nitrogen of the air.

Determinations of carbon made in mixtures of the soil samples collected in 1879 and in 1888 respectively show a very slight increase in the relation of carbon to nitrogen at the later date, the amounts being 11·73 carbon to one of nitrogen in 1879 and 11·77 in 1888.

Collection and Preparation of Soil Samples.—A steel frame 12 by 12 inches and 9 inches deep is driven down into the soil until its upper edge is level with the surface of the soil. All above ground vegetation is then cut off as closely as possible with scissors. The soil within the frame is then removed exactly to the depth of the frame and immediately weighed. It is then partially dried and mechanically separated by a series of sieves, all visible vegetable matter being, at the same time, picked out. The stones, the roots, and the remaining soil are thus separated, and the determinations of dry matter, nitrogen, &c., are made in the separated soil after being finely powdered. The loss of water at each stage of preparation and on drying the samples as analysed is also carefully determined.

The paper concludes with remarks on the botany of the meadow and the result of manuring and mowing on the order of predominance of the most prominent species in the mixed herbage. N. H. M.

Nitrates in the Rain of Tropical Districts. By A. MUNTZ and V. MARCANO (*Compt. rend.*, **108**, 1062—1064).—Recent researches having shown that soils and plants have the power of absorbing nitrogen directly from the atmosphere, determinations of the nitrates in rain-water are mainly valuable as evidence of the magnitude of atmospheric electrical discharges in the particular district.

The rain-water was collected in the manner previously described (*Compt. rend.*, **97**, 240) at Caracas, Venezuela, which is situated in latitude 10° 3′ N. at a height of 922 metres above sea-level. The temperature in this locality is very uniform, the mean being 21·8, rains are very irregular, and storms are frequent and violent. Sixty-three samples of rain were collected in 1883–4, and 58 in 1885. The results are expressed in milligrams of nitric nitrogen per litre—

July, 1883, to July, 1884..............	2·45 milligrams.
Jan., 1885, to Dec., 1885..............	2·01 „

The mean is 2·23, the minimum being 0·2, and the maximum 16·25 on October 19th, 1883. The mean result obtained by Boussingault at Liebfrauenberg, Alsace, was 0·18, and by Lawes and Gilbert at Rothamsted, England, 0·42. It is obvious that the quantity of nitric nitrogen in rain-water is much greater in tropical than in temperate regions, and the total weights of nitrogen which fall upon a given area show still greater differences because the depth of rain is so much greater in the tropics. Taking the annual rainfall at Caracas as 1 metre in depth, the weight of nitric nitrogen per hectare would be as follows:—

At Caracas	5·782 kilos.
At Liebfrauenberg	0·330 „
At Rothamsted	0·830 „

At St. Denis in the Island of Réunion, latitude 20° 5′ S., 19 specimens of rain collected by Raimbault in 1886–7 gave a mean of 2·67 milligrams per litre, the maximum being 12·5, and the minimum 0·4. This corresponds with a weight of 6·93 kilos. of nitric nitrogen per hectare.

It is evident that the quantity of nitric nitrogen in the rain of tropical districts is so large as to be of considerable practical importance. It is equivalent to 50 kilos. of sodium nitrate per hectare.

C. H. B.

Analytical Chemistry.

Technical Gas Analysis. By C. Winkler (*Zeit. anal. Chem.*, **28**, 269—289).—1. *Absorption of Carbon Monoxide.*—The author confirms the statement of Drehschmidt that a cuprous chloride solution which has absorbed much carbon monoxide will give up part of it again to another gas, and supports the proposal to always treat the gas twice with cuprous chloride, using on the second occasion a solution which has not previously absorbed more than traces of carbon monoxide. An ammoniacal solution of cuprous chloride shows the same tendency to part with the absorbed gas, although to a less degree, especially if kept for some time, in consequence of the slow oxidation of the dissolved monoxide.

Very minute quantities of carbon monoxide can be detected by absorption in cuprous chloride and subsequent addition of sodiopalladious chloride, when palladium separates as a finely-divided, deep-black precipitate. It is best to dissolve the cuprous chloride in a saturated solution of sodium chloride with a few drops of hydrochloric acid, and after absorption of the carbon monoxide to add water until cuprous chloride begins to separate (about 4 vols.) before adding the palladium solution. By this means 0·01 c.c. of the monoxide can be detected.

2. *Absorption of Heavy Hydrocarbons.*—Fuming nitric acid cannot be used for the absorption of ethylene or benzene in presence of carbon monoxide, since the latter is oxidised by fuming nitric acid, moreover, neither hydrocarbon is so perfectly absorbed by nitric acid or by bromine as by fuming sulphuric acid.

3. *Determination of Methane.*—The apparatus used is modified from that of Coquillion. A Hempel's tubulated gas-pipette is fitted with two stout wires of varnished brass passing through the cork, and reaching to about 2 cm. from the top. Their ends are connected

by a spiral of platinum wire, 0·35 mm. thick, heated by the current from two small Grove's cells. The whole is filled with water. The gaseous mixture, from which everything has been removed except hydrogen, methane, and nitrogen, is mixed with excess of air and passed over gently heated palladium-asbestos. The hydrogen alone burns, and its amount is known from the contraction. A further quantity of air is then added, sufficient for the combustion, if the gas consisted entirely of methane, and the mixture is then slowly drawn into the pipette, the electric circuit having first been closed. As soon as the water-level falls below the platinum spiral, combustion begins and proceeds quietly, and without danger, as the rest of the gas is drawn in. When completed, the gas is retransferred to the burette, the carbonic anhydride is absorbed, and the observed contraction, divided by 3, gives the amount of the methane. M. J. S.

Substitute for the Calcium Chloride Tube in Elementary Analyses. By J. Preusser (*Zeit. anal. Chem.*, **28**, 322—323).—This is an improvement on that of Schmitz (Abstr., 1885, 687), the gases passing first through sulphuric acid and then over phosphoric anhydride. It is in general shape like a U-tube, the first limb containing an inner vessel for the sulphuric acid. M. J. S.

Estimation of Nitrogen by Kjeldahl's Method. By E. Aubin and L. Alla (*Compt. rend.*, **108**, 960—961).—The authors summarise what they regard as the advantages of Kjeldahl's method, and lay special stress on its applicability to pasty and liquid substances, and to substances such as sewage, fæces, grain, &c., which are often not homogeneous, and cannot readily be powdered (compare this vol., pp. 648, 649, and 746). C. H. B.

Estimation of Nitric Nitrogen by Ferrous Sulphate. By Bailhache (*Compt. rend.*, **108**, 1122—1124).—The author prefers ferrous sulphate to ferrous chloride, because there is no danger of volatilisation of the ferric salt. The liquid also boils at a higher temperature, and expulsion of the nitrogen oxides is easier.

A small flask, holding 250 c.c., with a mark indicating this volume, is fitted with a cork which carries a short exit-tube drawn out to a point, and an acid funnel provided with a stopcock, the stem of the funnel reaching nearly to the bottom of the flask.

The following solutions are required: ferrous sulphate, containing 100 grams of the heptahydrated salt and 75 grams of concentrated sulphuric acid per litre; potassium dichromate, 17·85 grams per litre; sodium nitrate, 50 grams per litre; a cold saturated solution of sodium hydrogen carbonate. The ferrous sulphate and dichromate solutions are equivalent to one another and to 10·192 grams of sodium nitrate per litre.

50 c.c. of the standard ferrous sulphate is placed in the flask with about 25 c.c. of sulphuric acid, and the cork, with funnel, &c., is fitted in. 25 c.c. of the carbonate solution is introduced by means of the funnel, but before the whole of it has run in, 10 c.c. of the nitrate solution to be tested is placed in the funnel, and the addition of the

mixed liquids is regulated so that a uniform evolution of nitric oxide takes place. When the action has ceased, a further quantity of 25 c.c. of the carbonate solution is gradually added, and the unoxidised ferrous salt is determined by means of the dichromate. The results are satisfactory. C. H. B.

Quantitative Separation of Arsenic and Antimony. By O. Koehler (*Arch. Pharm.* [3], **27**, 406—409).—From a hot solution of arsenic and antimony in concentrated hydrochloric acid, hydrogen sulphide precipitates the arsenic completely, whilst the antimony remains in solution, provided the acid is present in sufficient excess, say two parts of concentrated acid to one part of antimonious chloride. The precipitated arsenious sulphide is filtered through a paper moistened with hydrochloric acid, and washed with dilute hydrochloric acid (1 : 3). The use of water would precipitate antimony either as sulphide or oxy-chloride. The arsenic precipitate is then oxidised with bromine-water and precipitated with magnesium solution. J. T.

Estimation of Sulphuric Acid in Presence of Iron. By P. Jannasch and T. W. Richards (*J. pr. Chem.* [2], **39**, 321—334).—Fresenius and Lunge have previously investigated this subject. The authors find that barium sulphate precipitated in presence of iron, and subsequently ignited, always weighs too little, and is more or less coloured with ferric oxide. The iron carried down in this way is least in amount when it exists in the original solution in the ferrous condition; its precipitation is not prevented by the presence of organic acids. Barium sulphate is only soluble in hot ferric chloride, and is deposited on cooling, so that this would not account for the low weight of the barium sulphate, which must, therefore, be due to loss of sulphuric anhydride during ignition. This was directly proved by igniting the precipitate in a current of air and absorbing the sulphuric anhydride in water; but inasmuch as barium sulphate does not lose weight when it is mixed with ferric oxide and ignited, that which is precipitated in presence of ferric salts must contain a double sulphate of iron and barium. A. G. B.

Oxidation Experiments with the Galvanic Current. By E. F. Smith (*Ber.*, **22**, 1019—1021).—The sulphur in copper pyrites can be entirely converted into sulphuric acid by means of a galvanic current (1 ampère). About 10 grams of potash is carefully heated in a nickel crucible until no more water-vapour escapes, and then kept melted by a small flame. The crucible is connected with the positive pole of a battery, and a platinum spiral in connection with the negative pole is dipped under the surface of the melted alkali. The powdered mineral is then thrown in and the circuit closed, whereon an energetic reaction takes place, and in 10 minutes oxidation is complete, the whole of the sulphur being converted into sulphuric acid. The cold melt is dissolved in water, the filtered solution acidified with hydrochloric acid, and the sulphuric acid estimated as barium sulphate. 0·1734 gram of the pyrites gave 32·35 per cent. of sulphur, whereas the same sample gave 32·54 per cent. with nitric acid and potassium chlorate. Attempts to oxidise iron pyrites in the same way were unsuccessful, but analyses of chrome-iron ore by this method gave 53 per cent. of chromic oxide in samples which, from analyses by the usual method, contained 54 per cent.

F. S. K.

Estimation of Thallium and Mercury. By W. Feit (*Zeit. anal. Chem.*, **28**, 314—322).—The method for estimating thallium is based on the titration of the iodine which separates when a thallic salt is mixed with potassium iodide. The solution is prepared for titration by adding sufficient sulphuric acid to convert all the thallium into sulphate, then bromine-water in small excess, and boiling to expel all the free bromine. To the cold solution, an excess of potassium iodide is added, next an excess of sodium hydrogen carbonate, and then a small measured excess of N/10 arsenious acid. The mixture is occasionally shaken until all the free iodine has disappeared, which sometimes requires a quarter of an hour. When the precipitate has acquired the pure yellow colour of thallous iodide, the mixture is made up and filtered, and an aliquot portion is titrated back with iodine and starch. Thiosulphate, in acid solution, can be used instead of arsenious acid. 506·15 parts of iodine (4 at.) corresponds to 407·2 parts of thallium (2 at.).

The estimation of mercury depends on the reduction of the precipitated oxides to metallic mercury by boiling with alkaline arsenite. The mercury is by preference brought to the state of mercuric salt by boiling with nitric acid, an excess of which does no harm. An excess, not too large, of soda is then added, followed by standard arsenious acid to the amount of a few c.c. more than corresponds with the mercury present. The mixture is then boiled for 5 or 10 minutes, cooled, made up, filtered from the mercury, and an aliquot part titrated with iodine after neutralising and adding sodium hydrogen carbonate. The oxidation by nitric acid of substances containing chlorides will liberate chlorine which will interfere with the result. Such solutions (for example, that of mercuric sulphide in aqua regia) should be treated with excess of sodium hydrogen carbonate, and then potassium iodide, until the mercuric iodide is redissolved. Any free iodine is reduced by sodium sulphite or arsenious acid and then, after adding starch, dilute iodine solution is cautiously added until the blue colour just appears. The solution is then fit for precipitation as above.

M. J. S.

Determination of Silicon and Iron in Cryolite. By R. Fresenius and E. Hintz (*Zeit. anal. Chem.*, **28**, 324—327).—When this fluoride is heated with sulphuric acid, the greater part of the silicon is left as a fine sand in the residue. The estimation can, however, be satisfactorily performed in the following manner. Three leaden U-tubes 19 cm. high (one of 2·6 and the others of 2 cm. bore) are connected air-tight by caoutchouc stoppers and narrow leaden tube. The wider one, standing in a sand-bath, is used as the decomposition vessel. The others contain ammonia, and are connected with a fourth U-tube of glass and an aspirator. A sulphuric acid bottle dries the air entering the decomposition vessel. About 5 grams of substance with 15 c.c. of sulphuric acid are placed in the decomposition tube. The aspirator is started, and the bath is heated to 200°, which temperature is maintained for two hours. The contents of the tubes are then washed out into a platinum basin, and heated with a few drops of hydrochloric acid; the undissolved residue, after washing, is fused with sodium carbonate. The aqueous solution of the melt is nearly neutralised hot with hydrochloric acid, and evaporated, whereby most of the silica is precipitated; the remainder is thrown down by solution of zinc carbonate in ammonia. Any of the fused mass insoluble in water is dissolved in hydrochloric acid and evaporated as usual. The contents of the lead absorption tubes are united and filtered. The washed residue, which contains lead sulphate, is extracted with ammonium acetate. The ammoniacal filtrate is mixed with excess of sodium carbonate, and the silica precipitated by ammoniacal zinc solution.

For the estimation of the iron, the cryolite is heated with sulphuric acid. The solution is separated and the residue fused with sodium carbonate. The melt is treated with water, evaporated with hydrochloric acid, and the acid solution added to the former. The iron is then oxidised by adding chlorine-water, and the solution is poured into hot potash. The precipitate is dissolved, and the iron is either determined volumetrically or thrown down by ammonium sulphide (after adding tartaric acid) and weighed as oxide. M. J. S.

Detection of Impurities in Alcohol. By P. CAZENEUVE (*J. Pharm.* [5], **19**, 513—515).—In 1882 (Abstr., 1882, 1002) the author published some important reactions for these impurities. Recently Barbet (*J. Pharm.* [5], **19**, 494) has written on the same subject, but has not noticed the effect of time and temperature on the reaction between these substances and potassium permanganate. As a standard of comparison the author employs pure alcohol of 93°, and a 1 : 1000 potassium permanganate solution; 10 c.c. of the standard alcohol at the temperature of the laboratory (15° to 20°) requires five minutes to give with 1 c.c. of permanganate a slightly yellowish rose tint, indicating that the reduction is not quite complete. An ordinary alcohol of 93°, under the same conditions, exercises a much more rapid reducing action, and this increased rate of action indicates impurity. If the test is applied to brandy, for example, it is necessary to compare with the standard alcohol diluted to the same strength. The test may be applied in the laboratory by distilling 500 c.c. over the water-bath. The first 10 c.c. of the distillate is compared with pure alcohol. When the distillation is finished, the last few c.c. in the retort is also tested for impurities of higher boiling point than alcohol. J. T.

General and Physical Chemistry.

Combustion of Organic Substances in Oxygen at High Pressure. By F. STOHMANN, C. KLEBER, and H. LANGBEIN (*J. pr. Chem.* [2], **39**, 503—537).—This paper contains a detailed description of the method of determining the heat of combustion of organic substances by burning them in oxygen at high pressure in a Berthelot's bomb (Abstr., 1887, 627); a good figure of the bomb is also given. The estimation of the constants of the apparatus is described at length, but no experiments other than those made for this purpose are mentioned.

The bomb consists of a steel crucible lined with platinum; into its mouth, which is made slightly conical, fits a lid, constructed of platinum underneath, of steel above; over this fits an outer steel lid, which screws on to the crucible, and so holds the inner lid tightly in position. This inner lid carries an apparatus for holding a small platinum crucible, containing a weighed quantity of the substance to be burnt; to the same apparatus a platinum wire is attached, and another platinum wire is attached to an insulated platinum rod, fitting air-tight in the lid of the bomb. To the ends of these platinum wires a small piece of fine iron wire is attached, a current passed through this causes it to melt, and the melted drops, falling on the substance in the crucible, usually bring about immediate combustion; if not, a small crystal of naphthalene of known weight is added, and the combustion of this generally inflames the other substance; the combustion is of an almost explosive character. Into the lid of the bomb a tube also is screwed, through which the oxygen is pumped in; this tube has a solid conical end, which acts as a valve, closing the apparatus when it is screwed down. The bomb has a capacity of about 300 c.c., weighs about 4080 grams, and has a water-equivalent of 350 grams. It is immersed in a cylindrical brass calorimeter 205 mm. long and 147 mm. in diameter: this weighs 566 grams, and has a water-equivalent of 52·5 grams. The water in it is stirred by a system of three parallel horizontal rings, of perforated brass plate, to which an up and down motion is communicated by clockwork; these weigh 225 grams, and have a water-equivalent of 15·9 grams. About 2075 grams of water is used in the calorimeter, so that the water-equivalent of the whole apparatus is 2500 grams. The oxygen is pumped in at a pressure of 24 atmospheres; about 10 grams is the amount that fills the bomb at this pressure; this oxygen is carefully purified from other gases, and also from particles of oil coming from the oil used to lubricate the air-pump. The thermometer used could be read to 0·001° or 0·002°.

In making an experiment, the bomb is immersed in the calorimeter, and the temperature read at intervals of one minute; as soon as successive readings differ by a constant amount, the current is passed through the iron wire, and the combustion takes place. With the stirrer in motion, it is found that in one minute 94 per cent., in two minutes 99·8 per cent. of the heat evolved is communicated to the water in the calorimeter, which rises in temperature usually about 3°. Readings are taken till successive ones differ by a constant amount, and a correction is made for loss of heat by radiation. The results seem to be very accurate; in a series of experiments made, the greatest deviation from the mean was 0·2 per cent. C. F. B.

Heat of Formation of Hyponitrites. By BERTHELOT (*Compt. rend.*, **108**, 1286—1288).—The action of bromine dissolved in potassium bromide on calcium hyponitrite in the proportion $CaN_2O_2,4H_2O + 4Br_2$, develops +41·40 Cals. When this number is corrected for the state of the bromine, it becomes +52·04 Cals. The action of excess of hydrochloric acid on calcium hyponitrite develops +6·41 Cals., and from the combined results it follows that the action of bromine on free hyponitrous acid, $H_2N_2O_2$ develops +45·63 Cals.

The heat of formation of the calcium salt will therefore be $H_2N_2O_2 + Ca(OH)_2$ diss. $+ 2H_2O = CaN_2O_2,4H_2O$ solid, develops + 31·6 Cals.

Similar experiments with the strontium salt lead to the conclusion that the action of bromine on free hyponitrous acid, develops +46·38 Cals., and $H_2N_2O_2 + Sr(OH)_2$ diss. $+2H_2O = SrN_2O_2$ solid, develops + 21·6 Cals.

Decomposition of the strontium salt by excess of potassium sulphate, leads to the conclusion that the neutralisation of hyponitrous acid by potassium hydroxide, develops + 7·8 Cals. per equivalent of the base.

From all the results it follows that N_2 gas + O gas + H_2O liquid in excess = $H_2N_2O_2$ diss., absorbs −57 4 Cals.

The difference between this number and the heat of formation of nitrous oxide, −20·6, is greater than the heat of neutralisation of the acid, a result which explains why nitrous oxide is not absorbed by alkaline hydroxides, and also why the hyponitrites so readily decompose with liberation of nitrous oxide. C. H. B.

Temperature of Transformation in Double Decomposition. By J. H. VAN'T HOFF and L. T. REICHER (*Zeit. physikal. Chem.*, **3**, 482—487).—When two salts which are capable of double decomposition are brought together in solution, of the four possible dissolved substances only three can generally be separated out in the solid form at the same time. If at the temperature of the experiment the product of the solubilities of the original two salts is less than that of the two resulting, the two former mixed with one of the latter separate out; in the reverse case, the two latter mixed with one of the former. There is, however, a certain temperature at which the products of the solubilities of both pairs of salts are equal, and at this temperature all four salts may separate out in the solid form. This is the temperature of transformation. It can usually be observed by the sudden contraction or expansion that here takes place. In the case of the reaction $Na_2SO_4,10H_2O + 2KCl = K_2SO_4 + 2NaCl +$

$10H_2O$, it was found to be 3·7°, and to be in agreement with that calculated from the solubilities of the salts. H. C.

Specific Gravity of Isomorphous Mixtures. By J. W. RETGERS (*Zeit. physikal. Chem.*, 3, 497—561).—The author employs the method described in a former paper (this vol., p. 812) for the investigation of the specific gravities of isomorphous mixtures. The mixtures taken are those of potassium and ammonium sulphates, of potassium and thallium alums, and of magnesium and iron sulphates, in all proportions. The methods of preparing and analysing crystals of the above mixtures are fully described, great care being taken to ensure uniformity of composition of the crystals used for each determination. The specific gravities are plotted against the percentage composition of each of the mixtures, and in all cases the curve obtained is a continuous straight line. This result is in accordance with the assumption that a mixed crystal of two isomorphous substances contains those substances in purely mechanical mixture. This, and a consideration of the other known properties of isomorphous mixtures, lead the author to define two substances as being truly isomorphous only when the physical properties of their mixed crystals are continuous functions of their chemical composition. H. C.

Determination of Affinity Coefficients. By W. HECHT and M. CONRAD (*Zeit. physikal. Chem.*, 3, 450—475).—This preliminary communication deals with the action of sodium ethoxide on methyl iodide as a special case of non-reversible reactions. The method of experimenting is described, and the method of applying the law of Guldberg and Waage in the present instance is discussed. It is demonstrated that the latter is fully applicable to the above reaction, and that the curve of decomposition is expressed generally by $k\theta = x\ (A - x)$, where k is the coefficient of affinity, and x is the amount of the original substance A decomposed in the time θ. It is also shown that variations in the relative amounts of sodium ethoxide and methyl iodide do not affect the constancy of k, but that the latter alters with the temperature in accordance with the equation $k_t = k_0 . 10^{\alpha t}$, in which α is a constant. H. C.

Dissociation of Electrolytes. By W. OSTWALD (*Zeit. physikal. Chem.*, 3, 588—602).—Some of the phenomena which accompany the formation of salts in solution are explained by the author on the dissociation hypothesis. When an acid and a base, each in dilute solution, are mixed, since in each, as likewise in the resulting salt, the ions are in the state of dissociation, no change in the condition of the metal or the non-metallic radicle will take place, but the sole alteration will be the combination of the free ionic hydrogen of the acid with the free ionic hydroxyl of the base to form water. Combination, therefore, does not, as formerly supposed, take place between the metal and non-metallic radicle, but only between the hydrogen and the hydroxyl, and to this one reaction must be referred all the phenomena accompanying the neutralisation of an acid by a base in solution.

The fact that the heat of neutralisation of all acids is the same, is thus easily explained, since in all cases only one and the same reaction occurs. The heat of neutralisation is, in fact, the heat evolved by the combination of ionic hydrogen with ionic hydroxyl, to which, in case the acid or base is not completely dissociated, must be added or subtracted the heat necessary to effect complete dissociation; this last is, however, in most cases inappreciable.

From the above it also follows that the addition of a solution of one salt to that of another, will be unattended by a development of heat, since in each, both before and after mixture, the ions are in a dissociated state. The displacement of a weaker by a stronger acid in a salt is due, not to the attraction of the metal for the non-metallic radicle, but to the attraction of the hydrogen of the stronger for the negative radicle of the weaker acid, combination between these two taking place, since a weak acid dissolves with little or no dissociation.

The author also considers apparently abnormal reactions between salts in solution, and shows that in all cases the reactions are only such as occur between the ions into which the dissolved salts are dissociated. A true double salt is defined as one which, on dissolving, is dissociated into the ions of the salts of which it is composed.

H. C.

Relation between the Affinity in Absolute Measure and Ostwald's Constants of Affinity. By J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, 3, 608—610).—As a measure of the affinity is taken the work which a reaction is capable of performing, and from the numbers given by Ostwald (this vol., p. 818) the affinity which effects the combination of the ions to form an acid is calculated. This work will be dependent on the concentration, but, as the author shows, in solutions of normal concentration, $A = 2T \log 1/k$, where T is the absolute temperature at which the constant of affinity k was determined, and A is the work, expressed in calories, which is effected by the formation of a kilogram-molecule of the acid from its ions in a cubic metre of the solution. The values of A for some of the more important acids examined by Ostwald are given, and the relations between affinity and constitution discovered by him are found to hold also for the new numbers. Trichloracetic acid gives a negative value for A, from which it must be assumed that the acid in a solution of double the normal strength is already more than half dissociated, so that at the normal concentration the affinity produces further separation of the ions and not the formation of acid. H. C.

Unit of Atomic Weights. By W. OSTWALD (*Ber.*, 22, 1721—1722). —A reply to Meyer and Seubert (this vol., p. 819).

Constitution of Alloys. By G. TAMMANN (*Zeit. physikal. Chem.*, 3, 441—449).—The molecular reduction of the freezing point of a solution D divided by the molecular weight M of the solvent should, according to Raoult, be a constant. If D be calculated by means of the well-known formula $D = 0{\cdot}0198\ T^2/w$, the above quantity D/M for ten different metals which the author has examined is by no means constant, but the results vary from 2·1 to 15. As this might be due to the general laws for other solutions not applying to solutions of metals in metals, a further examination of the freezing points of a number of amalgams and of sodium alloys was then made. The values for D obtained from dilute solutions of the metals in mercury are in all cases in general agreement with that calculated from the above formula, but for the solutions in sodium the observed numbers are in all cases very much smaller than the calculated value. The above results would in fact show that the molecules of dissolved metals in mercury consist only of single atoms, whereas in sodium, molecules of the same metals contain at least 3, and in some cases, as for instance for tin and palladium, as many even as 24 atoms. H. C.

Alloys. By P. Silow (*Zeit. physikal. Chem.*, 3, 605—607).—In this preliminary notice the author discusses the application of the laws which apply to other solutions to those of one metal in another. He calculates the molecular reduction of the solidifying points of some alloys by means of the two formulæ of Van't Hoff, $K(t-s)\sigma$, where t and s are the solidifying points of the pure metal and of the alloy, σ is the proportion of the dissolved metal in 100 parts of the solvent, K is its molecular weight, and $0{\cdot}02T^2/L$, where T is the absolute temperature at which the pure metal solidifies, and L is its latent heat of fusion. The results given by the two formulæ show a fair coincidence. H. C.

Determination of the Molecular Weight from the Rise in the Boiling Point. By E. Beckmann (*Zeit. physikal. Chem.*, 3, 603—604).—The results are given of the determination of the molecular weights of some organic compounds from the boiling points of their solutions in ether. The numbers obtained are in fair agreement with the theoretical. H. C.

Cryoscopic Behaviour of Solutions of Morphine Compounds in Benzene, Acetic Acid, and Water. By N. v. Klobukoff (*Zeit. physikal. Chem.*, 3, 476—481).—The cryoscopic behaviour of anhydrous morphine and morphine-derivatives is found to be a perfectly normal one. Hydrated morphine, $C_{17}H_{19}NO_3 + H_2O$, loses its water when dissolved in acetic acid, and hence the number for the molecular reduction is double the normal one. The same thing occurs with other hydrated morphine compounds. The hydrochloride and acetate in water seem to undergo complete dissociation into their ions, as in these cases also double the normal molecular reduction is obtained.
H. C.

Molecular Depression of the Freezing Point of Benzene by Alcohols. By E. Paternò (*Ber.*, 22, 1430—1433; compare this vol., p. 101).—Raoult (Abstract, 1884, 953) has stated that compounds containing hydroxyl-groups give, in benzene solution, a molecular depression only half as great as the normal. The author's experiments show that in dilute solutions the depression is either quite normal or approximately so, but that in more concentrated solutions it is quite abnormal. F. S. K.

Apparatus for Shaking. By J. Tafel (*Ber.*, **22**, 1868—1870).—The author describes with the aid of diagrams an apparatus by means of which a solid, liquid or gas, together or separately, can be gradually added to a liquid or semi-fluid substance, the whole being cooled or agitated constantly during the process. The apparatus consists of a large glass bottle of 5 to 6 litres capacity, placed with its long axis horizontally in a lacquered iron box which contains the cooling mixture. The neck of the bottle rests in a wooden bed, in an opening in the side of the box, and the lower extremity is surrounded by an iron cylindrical cap, which can be rotated by a cog-wheel placed outside the box. The bottle has a little play in the iron cap, the interstices being filled with paper, and it can be taken out of the box when necessary. The box is covered with a lid, the two halves of which can be opened separately, and is provided with an overflow and a cock by which it can be emptied. For introducing solid substances an inverted T-shaped tube is employed; one of the horizontal limbs passes into the centre of the bottle, the whole being supported by a wooden stand fastened on to an iron table projecting from the box. The vertical limb is filled with the substance, and a spiral passing the whole length of the horizontal limb and rotated by a system of wheels, gradually drives the substance forward. Gases or liquids are introduced through a separate tube, bent at right angles, and fastened to the three-way tube by means of india-rubber rings. The temperature is ascertained by a bent thermometer which passes almost to the lower side of the bottle, and is fastened to the three-way tube in the same way. The wheels are all connected by a driving rod, which passes through the box and is protected by a tube, and the speed of rotation of the spiral can be regulated to some extent, independently of that of the bottle, by altering the gearing. F. S. K.

Inorganic Chemistry.

Double Halogen Salts. By I. Remsen (*Amer. Chem. J.*, **11**, 291—319):—From a study of the double halogen salts, the author concludes that their composition is controlled by the following law: "When a halogen salt of any element combines with a halogen salt of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halogen salt is never greater and is generally less than the number of halogen atoms contained in the latter."

Double halogen salts not containing an alkali metal also follow this law, the only exception to which is the salt $Cu_2Cl_2,4KCl$.

Halogen salts must be regarded as being either acidic or basic, bearing the same relation to each other as the acidic and basic oxides do. The double salts, such as $NaAlCl_4$, are thus quite analogous to the double oxides of the same metals, such as $NaAlO_2$; two halogen atoms in the former playing the same part in linking the salts together as one atom of oxygen in the latter plays in linking the oxides together. The objection that the halogen atoms will have to be considered as polyvalent if his theory be correct has no weight in the author's opinion; for these elements must be polyvalent in their oxygen compounds, and in such compounds as ICl_3, IF_5, &c.

The nomenclature of the double halogen salts must be revised to render it analogous to that of the double oxides. A. G. B.

Atomic Weight of Oxygen. By G. S. Johnson (*Chem. News*, **59**, 272).—Noyes (this vol., p. 672) determined the atomic weight of oxygen by noting the amount of water formed by the action of hydrogen on a weighed quantity of copper oxide. The author points out that the method is subject to some sources of error, as shown by him (Trans., 1879, 232—244); two are certainly operative, namely, the retention of occluded hydrogen by incompletely re-oxidised copper and the retention of water by the reduced copper, as the temperature used by Noyes seemingly did not exceed 700° in the apparatus used. The other sources of error are due to the presence of sulphur in the copper; the sulphur is not expelled completely either during oxidation or reduction by hydrogen, and when the reduced copper is re-oxidised sulphuric acid forms. Sulphur is very generally present in commercial copper. D. A. L.

Absorptive Power of Water for Atmospheric Gases. By O. Pettersson and K. Sondén (*Ber.*, **22**, 1439—1446).—The authors have estimated, by means of the apparatus already described (compare p. 1034), the quantity of oxygen and nitrogen contained in pure water saturated with air; the results are given in the following table:—

Temperature of the water.	Found.			Calculated for absorption under 760 mm.		O per cent.
	Bar.	N.	O.	N.	O.	$100\frac{O}{N+O}$.
0·00°	772	19·85	10·15	19·53	10·01	33·88
6·00	771	16·58	8·39	16·34	8·28	33·60
6·32	741	16·20	8·18	16·60	8·39	33·55
9·18	729	14·96	7·60	15·58	7 90	33·60
13·70	771	14·37	7·24	14·16	7·14	33·51
14·10	770	14·35	7·15	14·16	7·05	33·24

When, in estimating the gases dissolved by water, the quantity of gas remaining after absorbing the oxygen and carbonic anhydride is greater than the quantity of nitrogen which could be absorbed at the temperature of the sample, the residual mixture must be exploded with oxygen and hydrogen in order to estimate the methane present.

The authors found 0·4—0·7 c.c. of methane per litre in spring water supplying the Stockholm water works and 0·2 c.c. per litre in the water of Lake Hammaiby. F. S. K.

Solubility of Oxygen in Water. By L. W. Winkler (*Ber.*, 22, 1764—1774).—In the method for estimating the solubility of oxygen in water already described (this vol., p. 79) no correction is made for the amount of oxygen dissolved in the reagents. The author finds that the amount present in the strong solutions of manganese chloride and caustic soda respectively are so small as to be negligable, but that sufficient oxygen is dissolved in the strong hydrochloric acid to introduce a small error into the results. To remove this dissolved oxygen, it is necessary to saturate the acid with carbonic anhydride and then boil to expel the gas, the process being repeated several times in an apparatus to which air cannot gain access. The solubility determinations were made with carefully distilled water, which was saturated at known temperatures with air carefully freed from carbonic anhydride, nitrous acid, and ammonia, and then titrated by the author's method. Drawings of the apparatus employed are given in the paper. In the calculation of the results, the author takes account of the height of the column of water in the absorption flask, and corrects for this by adding the equivalent in mm. of mercury of half the pressure exerted by this water-column to the barometric pressure, regarding the sum as the actual pressure under which absorption takes place. The amount of oxygen, C, dissolved by water under a pressure of 760 mm., is calculated by the formula $C = A(760 - f)/(B + d - f)$, where A is the amount of oxygen found in 1000 c.c. of water, B the barometric pressure, f the tension of aqueous vapour at the temperature employed, and d half the pressure of the water column in mm. of mercury. Determinations were made at intervals of about 5° between 0° and 30°, and concordant results were obtained; from these the solubility and absorption-coefficient of oxygen were calculated, the percentage of oxygen in air being taken as 20·96. The solubility, β', is defined as the quantity of gas (reduced to 0° and 760 mm.) dissolved by unit volume of a liquid under a pressure of 760 mm., and the absorption-coefficient, β, as the quantity dissolved when the pressure of the gas, independent of the tension of the liquid, amounts to 760 mm.; or in other words $\beta' = \beta(760 - f)/760$.

The mean values of C at temperatures approximating to 0°, 10°, 20°, and 30°, and the values calculated for the absorption-coefficient β were found to be :—

Temperature.	Mean value of C.	β.
0·15°	10·1454	0·048702
9·94	7·8842	0·038073
19·88	6·3697	0·031098
29·88	5·2664	0·026209

and from these data the absorption-coefficient and solubility of oxygen in water for each degree interval between 0° and 30° was calculated by means of the interpolation formula $\beta = 0{\cdot}04890 - 0{\cdot}0013413t + 0{\cdot}0000283t^2 - 0{\cdot}00000029534t^3$. The values calculated for the temperatures 5·20°, 5·65°, 14·78°, and 24·80° agree well with those obtained experimentally, and the absorption-coefficient is in every case higher than that found by Bunsen. W. P. W.

Autoxidation. By M. TRAUBE (*Ber.*, **22**, 1496—1514; compare Abstr., 1885, 1105; 1886, 661).—It has been previously stated as probable that the combustion of "bradoxidisable" substances (Abstr., 1883, 709) in organisms is brought about by ferments acting in a similar manner to the metals of the platinum-group, and that, amongst others, the contractile substances of the muscles may be looked on as oxygen-carriers of this nature. Hoppe-Seyler (*Zeit. physiol. Chem.*, 2, 22), on the other hand, considers that combustion in organisms is due to oxidation, brought about by the nascent hydrogen which is evolved in the fermentive processes; the nascent hydrogen decomposes the oxygen molecule, combining with one atom only, thus leaving the other free to oxidise. Zinc, iron, and other reducing agents, according to Hoppe-Seyler, act in like manner, and the formation of hydrogen peroxide by the slow combustion of these metals is the result of the oxidation of water by the liberated oxygen-atoms.

The author has already shown (*loc. cit.*) in previous papers that nascent hydrogen, and reducing compounds in general, do not bring about oxidation, and that, whenever such phenomena seem to occur, they are probably, or can be proved to be, due to the presence of oxygen-carriers. Hoppe-Seyler's hypothesis is therefore absolutely untenable.

When palladium hydride (about 1 gram) is shaken, in presence of air, with an aqueous solution of tetramethylparaphenylenediamine (36 c.c.), slightly acidified with sulphuric acid, the solution gradually becomes deep violet. If the mixture is shaken for five minutes only, the tetramine-derivative is not oxidised although hydrogen peroxide is formed; if the palladium hydride is then removed, the solution will remain colourless, but on adding a piece of ignited palladium or platinum an intense coloration is immediately produced, the metal acting as an oxygen-carrier between the hydrogen peroxide and the tetramethylparaphenylenediamine. Palladium and platinum are able to oxidise di- and tetra-methylparaphenylenediamine not only in presence of, but also in absence of hydrogen peroxide, provided that air be present.

When 1 per cent. zinc amalgam (25·992 grams) is shaken for 10 minutes, in presence of air, with 0·5 per cent. sulphuric acid (5 c.c.) containing crystallised oxalic acid (30 milligrams), the solution remains clear and hydrogen peroxide is formed, as can be proved by the titanic acid and zinc iodide-starch-copper sulphate reactions (compare Abstr., 1884, 1073). The solution now reduces more potassium permanganate than corresponds with the oxalic acid present, and assuming that the acid has remained unoxidised, the excess of permanganate employed showed that 1·37 milligrams of hydrogen peroxide had been formed. The zinc amalgam lost 62 milligrams of zinc, corresponding to 1·9 milligrams of hydrogen; this quantity of hydrogen, according to Hoppe-Seyler's views, should have been sufficient to oxidise 119·7 milligrams of oxalic acid, but not a trace of carbonic anhydride is evolved.

When liquid zinc amalgam (25 grams) is shaken for 10 minutes with 0·5 per cent. sulphuric acid (about 50 c.c.) containing oxalic acid (30 milligrams), in absence of air only 2 milligrams of zinc are dissolved, so that the solution of the zinc is considerably hastened by the presence of air.

Hydrogen peroxide (1·8 milligrams) is formed when liquid zinc amalgam (20 grams) is shaken for 10 minutes with air (300 c.c.), free from carbonic anhydride, carbonic oxide (300 c.c.), and 1 per cent. sulphuric acid (50 c.c.), but not a trace of carbonic anhydride is produced.

These experiments show that oxalic acid and carbonic oxide are not oxidised by nascent hydrogen in presence of air, and that hydrogen peroxide is formed in considerable quantities notwithstanding the presence of these compounds.

When palladium foil (4·6 grams) of about 32 cm. square in surface, and containing 280 c.c. of hydrogen, is shaken with water (50 c.c.) and air, the quantity of hydrogen peroxide formed is 0·9, 1·1, 1·3, and 1·5 milligrams after 30, 40, 50, and 60 minutes respectively. After 60 minutes the quantity of hydrogen peroxide present remains constant—as much being destroyed by the palladium hydride as is formed by the action of the oxygen. The same palladium foil gives, however, further quantities of hydrogen peroxide when shaken with fresh water. The formation of hydrogen peroxide continues until the solution contains about $\frac{1}{5000}$ of its weight of this compound, so that the absolute quantity produced increases with the quantity of water present. Hydrogen peroxide is formed immediately when palladium foil (5 grams), containing only 11 c.c. of hydrogen, is shaken with water and air, and a piece containing only 2 c.c. of hydrogen gives traces of hydrogen peroxide.

A piece of freshly ignited palladium foil (4·6 grams) of 32 cm. sq. in surface was placed in water (80 c.c.) containing hydrogen peroxide (80 milligrams) and a quantity of sodium indigosulphonate which would be destroyed by 0·15 milligram of active oxygen. Evolution of oxygen quickly commenced and after two days the whole of the hydrogen peroxide was destroyed, but the dye, although considerably decolorised, was not completely oxidised; almost the whole of the available oxygen (37·6 milligrams) was liberated in the form of gas, and not even 0·15 milligram combined with the colouring matter. In a second experiment, a piece of palladium (5 grams) of about 35 cm. sq. in surface, was placed in water (80 c.c.) containing a quantity of sodium indigosulphonate, which would require 0·07 milligram of oxygen for reduction, and hydrogen peroxide (0·5 milligram) was added daily. Each fresh addition of hydrogen peroxide was decomposed in 24 hours, but the dye was not decolorised until after 1·9 milligrams of available oxygen had been added. In a similar experiment, hydrogen peroxide (0·1 milligram) was added daily; the dye was completely bleached after adding 0·37 milligram of available oxygen. These experiments show that palladium acts as an oxygen-carrier between hydrogen peroxide and indigosulphonic acid, and that this action is most complete when the relative quantity of hydrogen peroxide in the solution is very small; in stronger solutions most of the peroxide is destroyed by the palladium with evolution of oxygen. If the solutions employed contained even less than 1/800,000 of their weight of hydrogen peroxide it is probable that the whole of the available oxygen would be carried to the indigosulphonic acid; such favourable conditions predominate in the slow action of air on palladium hydride. The presence of small quantities of sulphuric acid increases the quantity of oxygen carried by palladium, and the evolution of oxygen, even in relatively strong solutions of hydrogen peroxide, is diminished.

It has been previously shown that palladium hydride does not oxidise ammonia to nitrous acid in presence of air and water, although hydrogen peroxide is formed in considerable quantities (compare Abstr., 1883, 282). Hydrogen peroxide (0·5 milligram) was added daily to two 2 per cent. ammonia solutions (75 c.c.), in one of which a piece of freshly ignited palladium foil (5 grams) was placed. Oxygen was evolved from both solutions, the evolution being greater in the one containing palladium, but at the end of the seventh day neither ammonium nitrite nor nitrate was formed in either solution. In a second similar experiment, hydrogen peroxide (1 milligram) was added daily for five consecutive days; oxygen was evolved as before and, after four days, the solution free from palladium contained ammonium nitrite, but none was formed in the other solution even after six days. Concentrated ammonia (25 c.c.) was mixed with a 0·8 per cent. solution of hydrogen peroxide (25 c.c.), the mixture divided into two parts and freshly ignited palladium (4 grams) added to one of them. Oxygen was rapidly evolved from the solution containing palladium, and after 20 hours the whole of the hydrogen peroxide had been decomposed without a trace of nitrite having been formed. The hydrogen peroxide in the other solution was not entirely decomposed until after a few days and nitrous acid (2·8 milligrams) was formed. Similar experiments with dilute (1 per cent.) ammonia gave similar results. These experiments show that hydrogen peroxide alone oxidises ammonia in dilute or concentrated aqueous solution, the quantity of nitrite formed, though small in any case, increasing with the quantity of hydrogen peroxide employed; the greater portion of the hydrogen peroxide is, however, decomposed by the ammonia catalytically and oxygen is evolved. If palladium is present, the decomposition of the hydrogen peroxide is complete, even when it is added very gradually and is present only in very small quantities, the whole of the available oxygen being evolved. F. S. K.

Constitution of Peroxides. By M. TRAUBE (*Ber.*, 22, 1515—1517).—A reply to Richarz (Abstr., 1888, 12 and 769).

Formation of Hydrogen Peroxide from Persulphuric Acid. By M. TRAUBE (*Ber.*, **22**, 1518—1528).—To determine whether oxalic acid is oxidised by persulphuric acid (SO_4) in 70 per cent. sulphuric acid solution as stated by Richarz (*Ber.*, **21**, 1670), the author added a known quantity of oxalic acid, dissolved in 70 per cent. sulphuric acid, to 70 per cent. sulphuric acid containing a known quantity of persulphuric acid, and passed a stream of air, free from carbonic anhydride, through the mixture for three hours; not a trace of carbonic anhydride was evolved. The mixture was then made up to 100 c.c. with 70 per cent. sulphuric acid, and (1) the quantity of oxalic acid, (2) the total available oxygen, (3) the available oxygen in the hydrogen peroxide, and (4) the available oxygen in the persulphuric acid determined. The results showed that oxalic acid is not acted on by persulphuric acid in presence of 70 per cent. sulphuric acid, and that, in the first two or three hours, more than two-thirds of the persulphuric acid is decomposed, and its available oxygen almost completely converted into hydrogen peroxide. When the experiments described above occupied more than two or three hours carbonic anhydride was evolved, owing to the oxidation of the oxalic acid by the hydrogen peroxide; at low temperatures (8—10°), however, the evolution of carbonic oxide was very slight.

It was proved by similar experiments that carbonic oxide is not oxidised by a 70 per cent. sulphuric acid solution of persulphuric acid, and that within 3½ hours, more than two-thirds of the available oxygen is converted into hydrogen peroxide. As, therefore, persulphuric acid is such a feeble oxidising agent, it cannot be true that it oxidises water as is stated by Richarz (*loc. cit.*).

When a 40 per cent. sulphuric acid solution (20 c.c.) of persulphuric acid (= 16 milligrams of available oxygen), free from hydrogen peroxide, is diluted with water, neutralised with barium carbonate, and filtered, the filtrate contains hydrogen peroxide (= 7·4 milligrams of available oxygen); this experiment shows that Richarz's view (*loc. cit.*) that hydrogen peroxide is only formed from persulphuric acid in 70 per cent. sulphuric acid solution, is untenable.

Violet chromic sulphate is not oxidised to chromic acid by a 40 per cent. sulphuric acid solution of persulphuric acid; when chromic acid is treated with persulphuric acid in 70 per cent. sulphuric acid solution, it is reduced to chromic oxide in consequence of the formation of hydrogen peroxide.

Persulphuric acid also differs from other powerful oxidising agents in this, that in 70 per cent. sulphuric acid solution, it does not decompose but actually gives rise to hydrogen peroxide. Quantitative experiments showed that when hydrogen peroxide and persulphuric acid are present together in 40 per cent. sulphuric acid solution, they are both very slowly decomposed, equal molecules of the two compounds being destroyed, but a similar solution of either compound alone undergoes no considerable change within 48 hours.

Persulphuric acid does not act on organic compounds, or has, at the most, only a very slight action. In 40 per cent. sulphuric acid solution, it does not decolorise indigosulphonic acid until after half-an-hour's time, and a solution in dilute sulphuric acid (about 10 per cent.) can be filtered through paper without any reduction taking place. Neutral solutions of persulphuric acid are only very slowly reduced by alcohol, but arsenious acid is completely oxidised within a short time. Berthelot (Abstr., 1878, 469) has stated that arsenious acid is not acted on by persulphuric acid.

The following reactions show that persulphuric acid belongs to the class of oxygen molecule compounds (holoxides). Platinum, either in the form of wire or as platinum black, decomposes persulphuric acid with evolution of oxygen, but only in presence of acid. A neutral or slightly acid solution of persulphuric acid oxidises indigosulphonic acid only slowly, but immediately on adding ferrous sulphate. Persulphuric acid and hydrogen peroxide, when present together, behave like two holoxides. Persulphuric acid sometimes behaves as a reducing agent; a solution in 40 per cent. sulphuric acid, free from hydrogen peroxide, reduces lead peroxide, the hydrate of manganese dioxide, and silver peroxide.

The article concludes with a discussion of the existence of oxygen-molecule compounds which is principally controversial.

F. S. K.

Behaviour of Persulphuric Acid towards Nitrogen. Evaporation of Hydrogen Peroxide. By M. TRAUBE (*Ber.*, 22, 1528—1531).—Richarz has stated (Abstr., 1888, 12) that persulphuric acid, in 70 per cent. sulphuric acid, oxidises nitrogen to nitrous acid. The author finds that such is not the case. When a solution of (1) persulphuric acid (= 48 milligrams of available oxygen), (2) nitrous acid (1·3 milligrams), (3) hydrogen peroxide (10 milligrams), in 70 per cent. sulphuric acid, is placed in a flask and the air inside tested with paper strips moistened with various reagents, the colorations produced are identical in the experiments with persulphuric acid and hydrogen peroxide, whilst those obtained with the nitrous acid solution are quite different. These results show that nitrogen is not oxidised by persulphuric acid, that hydrogen peroxide is slightly volatile at the ordinary temperature, and that the air above a mixture of persulphuric acid and 70 per cent. sulphuric acid contains hydrogen peroxide in a state of vapour.

Water (10 c.c.) containing hydrogen peroxide (200 milligrams) was placed in a closed flask of 200 c.c. capacity in which were suspended papers moistened with (A) zinc iodide, starch and ferrous sulphate, (B) zinc iodide and starch, (C) titanic acid. A was coloured immediately, B after 15 seconds, and C after 6 minutes; when the papers were dry, the reactions did not appear for considerably longer periods. With aqueous solutions (10 c.c.) containing hydrogen peroxide (10 milligrams), the moist papers (A, B, C,) were coloured in 0·5, 8 and 12 minutes respectively. In similar experiments with 70 per cent. sulphuric acid (10 c.c.) containing hydrogen peroxide (1 milligram), B was coloured yellow in six hours, but the other two papers showed no reaction. F. S. K.

New Hydrate of Sulphuric Acid. The Nature of Solution. By S. U. PICKERING (*Chem. News*, 60, 68).—This communication announces the isolation of a new hydrate of sulphuric acid, the existence of which in solution the author had determined from a study of the densities and heat of dissolution of solutions of the acid (Proc., 1889, 88). The hydrate is $H_2SO_4,4H_2O$. It is a crystalline solid melting at −25°. Any excess of acid or of water lowers its melting point considerably. S. U. P.

Sulphites and Thiosulphates. By H. SCHWICKER (*Ber.*, **22**, 1728—1737).—*Sodium potassium sulphite*, $NaKSO_3 + 2H_2O$, separates in yellowish crystals, when a concentrated solution of potassium hydrogen sulphite is neutralised with the calculated quantity of sodium carbonate, and evaporated over sulphuric acid. (Compare Röhrig, *J. pr. Chem.* [2], **37**, 250.) When heated with ethyl iodide at 140°, it yields a compound $4SO_2Et{\cdot}OK,NaI$, which crystallises from hot alcohol in colourless needles.

Potassium sodium sulphite, $KNaSO_3 + H_2O$, prepared from sodium hydrogen sulphite and potassium carbonate in like manner, is a yellowish, crystalline compound. When heated with ethyl iodide at 140°, it gives a colourless salt, which has the composition

$$4SO_2Et{\cdot}ONa,KI.$$

The salt $HKNa_2(SO_3)_2 + 4H_2O$, separates in large, well-defined plates, when a solution of equivalent quantities of sodium potassium sulphite and sodium hydrogen sulphite, or a solution of sodium hydrogen sulphite (2 mols.) and potassium carbonate (0·5 mol.) is evaporated. It is moderately stable in the cold, but it is quickly decomposed when heated. It is readily soluble in water, the solution having an acid reaction, and concentrated solutions combine with acetone with development of heat. Compounds of the same composition, and which seem to be identical with the double salt just described, are obtained when a solution containing sodium sulphite and potassium hydrogen sulphite is evaporated, or when a hot solution of either of the sodium potassium sulphites (see above) is saturated with sulphurous anhydride; the solubility in water of all these compounds is approximately the same (69 per cent. at 15°), but in some respects they differ slightly.

The compound $HNaK_2(SO_3)_2 + 3H_2O$ separates in transparent prisms when a concentrated solution of equivalent quantities of sodium potassium sulphite and potassium hydrogen sulphite is evaporated over sulphuric acid; it behaves like the double salts described above.

A compound, $H(NH_4)Na_2(SO_3)_2 + 4H_2O$, separates in colourless crystals when ammonia is passed into a concentrated solution of sodium hydrogen sulphite, or when a concentrated solution of ammonium hydrogen sulphite is partially saturated with sodium carbonate. Tauber (*Jahresb. Chem. Techn.*, 1888, 444), by the latter method, obtained a salt to which he assigned the formula $2Na_2SO_3,(NH_4)_2S_2O_5 + 10H_2O$, and, in fact, all the double salts described above may be regarded as pyrosulphites of analogous constitution. It crystallises in large plates, and is moderately stable at the ordinary temperature, but at 130° it is quickly decomposed with evolution of water, ammonia, and sulphurous anhydride. It is readily (48·5 per cent. at 15°, 42·3 per cent. at 12·4°) soluble in water, and the solution has an acid reaction. It seems to be identical with the double salt described by Marignac (*Jahresb. Chem.*, 1857, 118).

Sodium potassium thiosulphate, $SNa{\cdot}SO_2{\cdot}OK + 2H_2O$, is obtained in large, transparent plates, when a freshly prepared, concentrated solution of ammonium pentasulphide is added to a solution of sodium potassium sulphite (see above) until a permanent yellow coloration is produced, the ammonia expelled by boiling, and the filtered solution evaporated on the water-bath. It is very readily (213·7 per cent. at 15°) soluble in water, melts at about 57°, and when heated with ethyl bromide in aqueous solution it yields colourless crystals of potassium ethyl thiosulphate.

Potassium sodium thiosulphate, $SK{\cdot}SO_2{\cdot}ONa + 2H_2O$, prepared from potassium sodium sulphite (see above) in like manner, crystallises in small, colourless plates, melts at about 62°, and is very readily (105·3 per cent. at 15°) soluble in water. When an aqueous solution is heated with ethyl bromide, sodium ethyl thiosulphate is obtained; the last-named compound crystallises from dilute alcohol in long, transparent needles which seem to contain 1 mol. H_2O.

Potassium tetrathionate is obtained when either sodium potassium or potassium sodium thiosulphate is treated with iodine; this abnormal behaviour is owing to the fact that potassium iodide decomposes sodium tetrathionate with formation of the more stable and more sparingly soluble potassium salt. When iodine is added to a solution of sodium thiosulphate containing a sufficient quantity of potassium iodide, potassium tetrathionate is alone formed.

The compound $KAgS_2O_3 + NH_3$ separates in nacreous plates when a solution of either of the sodium potassium thiosulphates, or of potassium thiosulphate, is mixed with an equivalent quantity of an ammoniacal silver nitrate solution. It is very sparingly soluble in water, and silver sulphide quickly separates from the solution, but it dissolves freely in hot ammonia, and crystallises from the cold solution in large plates. It is stable at the ordinary temperature, but at 100° ammonia is evolved, and a grey powder remains. When a solution of sodium thiosulphate is mixed with ammoniacal silver nitrate, no precipitation occurs, but, on adding potassium chloride or potassium nitrate, the compound just described separates in nacreous plates.

Sodium silver thiosulphate, $NaAgS_2O_3 + H_2O$, is obtained in large, well-defined, monoclinic plates, when a solution of equivalent quantities of sodium thiosulphate and ammoniacal silver nitrate is evaporated over sulphuric acid (compare Lenz, *Annalen*, **40**, 94). It decomposes only slowly at the ordinary temperature, but immediately on heating; at 100° only water is evolved, and a grey, crystalline powder remains. It is very sparingly soluble in water, and the solution is unstable, but it dissolves freely in cold ammonia, and on adding alcohol a colourless flocculent compound, probably $NaAgS_2O_3 + NH_3$, is precipitated.

It follows from the above experiments that both sulphites and thiosulphates have an asymmetrical constitution. F. S. K.

Behaviour of Sodium Thiosulphate with Acids. By W. VAUBEL (*Ber.*, **22**, 1686—1694).—The author having noticed that by the decomposition of this salt by acids, small quantities of hydrogen sulphide were sometimes formed, have carefully studied its behaviour towards acids. With formic, acetic, succinic, citric, hydrobromic, hydriodic, hydrofluoric, nitric, sulphurous, dithionic, phosphoric, and very dilute sulphuric acids, the amount of sulphurous anhydride and sulphur obtained always agrees with that required for the equation $Na_2S_2O_3 + 2AcOH = 2AcONa + H_2O + SO_2 + S$. But with stronger sulphuric acid this is not the case. In a series of experiments where 10 mols. of sulphuric acid of various degrees of concentration were employed to 1 mol. of sodium thiosulphate, and the reaction completed in the cold, the sulphurous anhydride evolved varied from 74 per cent. of the theoretical with acid of 20 per cent. to 92 per cent. with acid of 90 per cent., the precipitated sulphur more nearly approached the theoretical quantities. But with 100 per cent. sulphuric acid, the percentage of sulphurous anhydride fell to 45·4 per cent., that of precipitated sulphur to 9·15 per cent., whilst much less than the theoretical quantity of sulphuric acid was neutralised. In the last-named reaction the evolution of hydrogen sulphide was very noticeable. With more dilute acid, it was often detected, but was estimated with the sulphurous anhydride.

When these experiments were repeated with 10 per cent., 20 per cent., and 40 per cent. hydrochloric acid, the sulphurous anhydride varied between 82—88 per cent. of the theoretical, that of precipitated sulphur between 86 and 97 per cent., whilst quantities of sulphuric acid corresponding with 6 to 8·5 per cent. sulphur were always formed.

Geuther showed that when a solution of sodium thiosulphate is treated with silver oxide, silver sulphide is formed, and the author finds that the quantities so formed correspond exactly with those required for the equation $Ag_2O + Na_2S_2O_3 = Ag_2S + Na_2SO_4$. Orlowski has shown (*J. Russ. Chem. Soc.*, 1883 [i], 32) that those elements precipitated by hydrogen sulphide in acid solutions are also under like conditions precipitated as sulphides by sodium thiosulphate.

From these results the author concludes that the decomposition of thiosulphuric acid is not the simple one generally believed, but that the first phase is a decomposition into hydrogen sulphide and sulphuric anhydride, which then further react on each other. The various reactions taking place would then be expressed by the equations:— (I) $H_2S_2O_3 = H_2S + SO_3$. (II) $H_2S + SO_3 = SO_2 + S + H_2O$. (III) $2H_2S + SO_2 = 3S + 2H_2O$. (IV) $3H_2S + SO_3 = 4S + 3H_2O$.

L. T. T.

Hyponitrites. By MAQUENNE (*Compt. rend.*, **108**, 1303—1306).—The hyponitrites at present known are the silver, barium, and ethyl salts, but the first two are unstable, and the latter is extremely explosive. The strontium and calcium compounds, however, are much more stable.

Calcium hyponitrite.—Crude silver hyponitrite is treated with calcium chloride in presence of a small quantity of nitric acid, and the filtered liquid is mixed with ammonia. Calcium hyponitrite separates as a brilliant crystalline powder, which attaches itself to glass after the manner of magnesium ammonium phosphate. It has the composition $CaN_2O_2 + 4H_2O$, and is almost insoluble in water, but dissolves readily in dilute acids. When heated at 100°, it effloresces and evolves gas; when treated with sulphuric acid, it evolves nitrous oxide, and when treated with bromine it is oxidised to the nitrate.

Strontium hyponitrite, $SrNrO_2 + 5H_2O$, is obtained in a similar manner; if heated at 100°, it effloresces with very slight evolution of gas.

Calcium aceto-hyponitrite, $CaN_2O_2,Ca(C_2H_3O_2)_2 2AcOH + 4H_2O$, separates in small, white needles, when the calcium hyponitrite is added in successive small quantities to acetic acid of about 30 per cent., until the salt ceases to dissolve. It dissolves in water, forming a very slightly acid solution. Raoult's cryoscopic method gave for this salt a molecular reduction of 104, and for Villiers's sesquiacetate a molecular weight of 68. It follows that the two compounds are not analogous; it would seem also that the true formula of hyponitrous acid is $H_2N_2O_2$ and not HNO.

Strontium aceto-hyponitrite crystallises with 3 mols. H_2O, closely resembles the calcium salt, and is obtained in a similar manner. *Barium aceto-hyponitrite* has a strictly analogous composition, but is much less stable.

These results confirm the empirical composition attributed to hyponitrous acid by Divers, but indicate that the empirical formula ought to be doubled in order to represent the molecule.

C. H. B.

Solubility of Arsenious Oxide and Arsenious Sulphide. By K. CHODOUNSKY (*Chem. Centr.*, 1889, 569, from *Listy. Chem.*, **13**, 114—117).—Recrystallised arsenious oxide dissolved in the following proportions, at 18·5°: 100 parts pure aqueous solution contained 0·8507 gram; 100 c.c. containing 1·3195 gram hydrogen chloride, 1·1513 gram; 100 c.c. containing 6·09 grams hydrogen chloride, 1·2724 gram; 100 c.c. hydrochloric acid, 1·4529 gram arsenious oxide. Although arsenious oxide is soluble in dilute sulphuric and acetic acids, no regularity in the solubility was observed. The solubility appears to increase in the same ratio with equal increment of temperature in acid solutions of different strengths; 100 c.c. of dilute sulphuric acid dissolved 1·0915 gram at 80°, and 0·5422 gram at 18·5°; 1·3664 gram at 80°, and 0·7203 gram at 18·5°; 1·1933 gram at 80°, and 0·6522 gram at 18·5°; the ratios being 2·01 : 1, 1·89 : 1 and 1·84 : 1 respectively. The author also found that the small quantity of arsenious sulphide which dissolves in pure water gradually decomposes with liberation of hydrogen sulphide. The freshly precipitated sulphide appeared to be most prone to suffer in this manner, to the extent of 1·5 to 6 per cent., according to the acidity and temperature. This decomposition is much reduced by boiling the solution, and the author infers that there is one modification of arsenious oxide soluble in water, and which forms hydroxysulphide.

J. W. L.

Presence of Sodium Sulphate in the Atmosphere, and the Origin of Saline Powders. By P. M. DELACHARLONNY (*Compt. rend.*, **108**, 1307).—The author has previously shown that when saline solutions evaporate minute particles of the dissolved salts are carried into the air (Abstr., 1887, 211), and he considers that this is the true cause of the presence of minute particles of sodium sulphate and other salts in the atmosphere (compare Parmentier, this vol., p. 826). C. H. B.

Dissociation of the Sulphides of Cadmium and Zinc by Means of Metallic Cadmium and Zinc. By H. N. MORSE and J. WHITE (*Amer. Chem. J.*, **11**, 348—351).—In a previous paper (this vol., p. 755), the authors described the dissociation of the oxides of cadmium and zinc by their respective metals; they now detail their experiments with the sulphides. The methods of conducting the experiments, and the results obtained are exactly similar to those already described in the case of the oxides (*loc. cit.*).

The oxides appear to begin to dissociate at a somewhat lower temperature than the sulphides. Of the two oxides, zinc oxide appears to dissociate the more readily; of the two sulphides, the cadmium sulphide. A. G. B.

Modifications of Precipitated Cadmium Sulphide. By N. v. KLOBUKOFF (*J. pr. Chem.* [2], **39**, 412—425; compare Abstr., 1888, 224).—To ascertain whether the red modification of precipitated cadmium sulphide is a real isomeride, or only a physical isomeride of the yellow modification, the author has determined—(1) their specific gravities, which vary between 3·906 and 4·147 for the yellow, and between 4·476 and 4·513 for the red; (2) their crystalline form, which is hexagonal in the yellow variety, but two or more different forms in the red; this makes it probable that there are more than two varieties; (3) their behaviour under friction, pressure, chemical agents, &c.; under these influences, the yellow changes into the red.

These results tend to show that the yellow and red varieties are real isomerides, possibly polymerides. A. G. B.

Occlusion of Gases by Electrolytic Copper. By A. SORET (*Compt. rend.*, **108**, 1298—1300; see this vol., p. 105).—A 25 per cent. solution of the copper salt was used, either neutral or containing free acid in amount varying from 0·1 to 0·9 of an equivalent. The current did not exceed 0·5 ampère, the electrodes being 40 sq. cm. in area, and the distance between them 50 mm. The temperatures varied from 10° to 40°; some of the experiments, however, being made at 2°. Electrolysis usually continued for 24 hours, the anode consisting of copper of good quality. In order to estimate the occluded gas, the deposited metal was heated in a vacuum in doubly glazed porcelain tubes. Carbonic anhydride comes off even below a dull red heat, but hydrogen comes off but slowly at dull redness, six to eight hours' heating being required for 10 to 15 grams of metal.

The ratio between the volume of gas occluded and the weight of copper deposited decreases as the weight of the deposit increases, but the proportion of carbonic anhydride increases. For the same weight of metal, the quantity of gas occluded diminishes as the temperature rises. Increase in the amount of free acid increases the amount of gas occluded, and the deposit is less compact. In neutral solutions, the proportion of carbonic anhydride in the occluded gas is always greater than in presence of free acid, and it increases rapidly with the temperature up to 30°, at which point it constitutes 90 per cent. of the gas. After some hours, the deposit becomes dendritic, especially at the edges, the dendrites being long and very fragile. In a very few cases, carbonic oxide was found in the gas, but in all probability it results from a secondary reaction between the hydrogen and the carbonic anhydride in the process of extraction.

Electrolytic copper occludes only hydrogen and carbonic anhydride, the former being usually, and in presence of free acid invariably, in the greater proportion. The fragility of the deposit is correlated with the presence of excess of occluded carbonic anhydride.

C. H. B.

New Reaction with Ferric Chloride. By L. GABBA (*Chem. Centr.*, 1889, 667, from *Rend. R. Inst. Lombardo* [2], **22**, 238—239).—A concentrated solution of ferric chloride reacts with finely-divided plumbic sulphide, ferrous chloride, plumbic chloride, and sulphur being the products. The reaction takes place quickly in the cold, and very quickly when warmed gently, and is not restricted to the precipitated sulphide, the change being effected with finely-pulverised galena, not more than 1 per cent. remaining unacted on.

J. W. L.

Titanium Compounds. By T. KOENIG and O. v. D. PFORDTEN (*Ber.*, **22**, 1485—1494; compare Abstr., 1888, 788).—When excess of titanic acid is treated with cold, concentrated hydrochloric acid, and, after keeping for a few days, the clear supernatant liquid evaporated under reduced pressure, colourless crystals of titanic acid hydrochloride are obtained. This compound is soluble in water, and contains titanium and chlorine in the proportion of 1 : 1·47.

A comparison of the behaviour of a concentrated solution of the dichloride $TiCl_2(OH)_2$ previously described (*loc. cit.*) with that of a solution of titanic acid hydrochloride, towards ether, showed that the two compounds are not identical.

When a few drops of concentrated hydrochloric acid are added to a strong solution of titanic acid hydrochloride, an oxychloride is precipitated, but it redissolves on adding more hydrochloric acid; the solution then behaves like a solution of the dichloride.

When finely-divided titanic iron is heated for several hours with concentrated sulphuric acid, it turns dark blue, and becomes covered with a fine white powder (compare Sheerer, *Ann. Phys. Chem.*, **64**, 489); the solution contains iron, but no titanium salt as stated by Glatzel (this Journal, 1877, i, 688). The natural ore undergoes no change when ignited in a stream of pure, dry carbonic anhydride, and, as Wiegand has already shown, ferrous oxide and titanium sesquioxide can exist together in solution; these facts show that no change of titanium sesquioxide and ferric oxide into titanic acid and ferrous oxide, such as has been assumed by Groth, takes place when the mineral is treated with hot sulphuric acid.

Menaccanite and titanic iron from Egersund and Snarum were heated in a stream of pure hydrogen, the loss ascertained, the residue boiled with dilute sulphuric acid or acetic acid, and the residual titanium compound ignited in the air, after washing with water, alcohol, and ether consecutively. The loss of weight (12·23—12·33 per cent.) on reduction agreed with the mean loss (12·96 per cent.) shown by the equations—

$$7TiO_3Fe + 18H = Ti_7O_{12} + 7Fe + 9H_2O, \text{ and}$$
$$TiO_3Fe + 2H = TiO_2 + Fe + 2H_2O,$$

and the subsequent increase on igniting in the air was 2·15—2·53 per cent. If titanic iron has the formula Ti_2O_3,Fe_2O_3, the loss on reduction should be 15·7 per cent. in accordance with the equation—

$$Ti_2O_3,Fe_2O_3 + 6H = Ti_2O_3 + 2Fe + 3H_2O,$$

and the subsequent increase on oxidation 11·11 per cent. Similar experiments were made employing hydrogen sulphide instead of hydrogen; the increase in weight (9·43—9·73 per cent.), after igniting in the gas, agreed with the change of TiO_3Fe into TiO_2 + FeS, which requires 10·53 per cent., whilst the conversion of Ti_2O_3,Fe_2O_3 into Ti_2O_3 + 2FeS requires 5·26 per cent. After removing the ferrous sulphide and any sulphur present, the residue increased only 0·97 per cent. on ignition.

Ferric orthotitanate, $Fe_4(TiO_4)_3$, is obtained when titanic acid and anhydrous ferrous fluoride are heated together with a large quantity of sodium chloride; ferrous titanate is not formed (compare Hautefeuille, *Compt. rend.*, **59**, 733). On ignition in hydrogen, ferric orthotitanate behaves like titanic iron, and is converted into iron and titanic acid. When warmed with concentrated sulphuric acid, it turns green, and on diluting the whole dissolves; the solution contains titanic acid and ferric sulphate, but no ferrous salt. F. S. K.

Ammoniacal Derivatives of Ruthenium. By A. Joly (*Compt. rend.*, **108**, 1300—1303).—By boiling the so-called ruthenium ammonium chloride with excess of ammonia, Claus obtained a compound to which he gave the formula $RuCl_2,4NH_3 + 3H_2O$. The author has shown, however, that the double chloride is really a nitrosochloride (this vol., 352 and 678), and he finds that Claus's compound and all the salts derived from it are represented by the general formula $RuX_2{\cdot}NO{\cdot}OH,4NH_3$, where X is a halogen or acid radicle.

If ammonium ruthenium nitrosochloride is boiled for a long time with excess of ammonia, the liquid becomes golden-yellow, and deposits yellow or orange-yellow anhydrous crystals of the composition $RuCl_2{\cdot}NO{\cdot}OH,4NH_3$. No gas is evolved. If the solution is not sufficiently dilute, the reaction is incomplete. The bromide and iodide are obtained in a similar manner, and the solubility of these haloïd compounds decreases as the atomic weight of the halogen increases. They are isomorphous, and form monoclinic prisms; in the case of the chloride $a : b : c = 1·5565 : 1 : 1·4647$ and $ph' = 78° 45'$. The *platinochloride*, $RuCl_2(NO)OH,(NH_3)_4,PtCl_4$, forms an orange-yellow, crystalline powder, almost insoluble in cold water.

The nitrate is obtained from the chloride by the action of silver nitrate, or by adding a warm concentrated solution of the chloride to an excess of nitric acid. It is only very slightly soluble in cold water, and practically insoluble in concentrated nitric acid. It crystallises in yellow monoclinic prisms; $a : b . c = 1{\cdot}41492 : 1 : 1{\cdot}37734$, and $ph' = 68° 18'$.

The *sulphate* and *carbonate* are obtained from the chloride by the action of the corresponding silver salts. The carbonate crystallises with 2 mols. H_2O. The sulphate crystallises with 1 mol. H_2O, and is the most soluble of all the salts. It forms simple, well-defined triclinic prisms; $a : b : c = 1{\cdot}63014 : 1 : 1{\cdot}28274$, $ab = 83° 33'$, $bc = 110° 12'$, $ca = 114° 4'$.

The action of silver hydroxide on the chloride yields a strongly alkaline liquid, which decomposes when concentrated, and leaves a brown residue which, according to Claus, contains 2 mols. NH_3. Its proper formula will therefore be $Ru(NO)(OH)_3,2NH_3 + H_2O$. The author was unable to obtain any salts of this series in a crystalline condition.

It is evident that the ammoniacal derivatives of ruthenium are not analogous to those of any other platinum metal. C. H. B.

Organic Chemistry.

Burmese Petroleum. By R. Romanis (*Chem. News*, **59**, 292).—Petroleum from wells in the Irawaddy group east of the Arracan Yoma, varies even in neighbouring wells; it is generally a viscid liquid, sp. gr. from 0·85 to 0·90, with strong green fluorescence, and solidifies at about 24°. It contains gas, benzene, and solid paraffin in solution. The flashing point of the fresh oil is about 3° or 4° above the melting point, but when conveyed in ordinary barges to Rangoon, the flashing point becomes 35° higher, owing to loss of volatile constituents, which loss does not take place in tank barges. When refined at Rangoon, it yields about 30 per cent. of burning oil (flashing point 36°), the same quantity of lubricating and batching oil, and 5 per cent. of solid paraffin. Oil from the other district in Burma, west of the mountains in the province of Arracan, comes from wells in the Brongas Islands, and near Kyank-Pyn. The former is a reddish-brown limpid liquid, of sp. gr. 0·825 at 32°; the flashing point by Abel's test is 40°; it contains benzene and analogous hydrocarbons, and does not solidify. The following result was obtained by the fractional distillation of a sample of Arracan oil. Gas was evolved at 30°; liquid began to distil at 70°:—

70— 90°	3·1	per cent.
90—100	7·6	,,
100—130	10·6	,,
130—200	18·7	,,
200—300	18·7	,,
Above 300°	12·5	,,
Oil left in retort	8·0	,,
Paraffin crystals	3·1	,,
Total	82·3	,,

and by distilling with steam—

100°	23·3 per cent.
100—110°	33·0 ,,
110—130	29·3 ,,
Residue	13·3 ,,
	98·9

D. A. L.

Pentamethylene and Tetramethylene Bromides. By G. Gustavson and N. Demjanoff (*J. pr. Chem.* [2], **39**, 542—543).—The authors prepared pentamethylenediamine by Ladenburg's method. Trimethylene cyanide was dissolved in absolute alcohol, and reduced with sodium. The alcohol was distilled off, and pentamethylenediamine was driven over from the residue with superheated steam. The aqueous solution thus obtained was evaporated to dryness, and treated with water and silver nitrate; it was then filtered, and the water distilled off. On distilling the residue under a pressure of 31 mm., pentamethylene glycol came over at 162°. It was found that the glycol distilled unchanged under the ordinary pressure at 260°. It was heated in a sealed tube at 100° with excess of fuming hydrobromic acid; the liquid separated into two layers, the lower of which consisted of nearly pure pentamethylene bromide,

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3{\cdot}CH_2Br.$$

This, when purified, boiled at 204—206°.

Tetramethylene bromide, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, was prepared in the same way from ethylene cyanide, but the yield was much smaller in this case; it boils at 188—190°.

The authors remark that these penta-, tetra-, &c., methylene bromides and glycols boil at considerably higher temperatures than the substances isomeric with them. C. F. B.

Formation of Hexylacetylene from Methylvalerylacetylene. By A. Béhal (*Bull. Soc. Chim.*, **50**, 629—631; compare Abstr., 1888, 929).—The author heated caprylidene (12 grams), prepared by the action of dry potassium hydroxide on caprylene bromide, with sodium (2·3 grams) in a sealed tube at 100—110° for 36 hours. After exhausting the resulting gelatinous product with benzene, the solvent was distilled off, and 9 grams of a liquid boiling between 125° and 135° was obtained. This precipitates from ammoniacal cuprous chloride a yellow cuprous caprylidenide. It appears, then, that the presence of sodium has determined the conversion of a substituted into a normal acetylene. T. G. N.

Ferricyanides. By C. Rammelsberg (*J. pr. Chem.* [2], **39**, 455—464).—The author has reinvestigated the lead ferricyanide compounds, and has obtained the same compounds as those described by Schuler (Abstr., 1879, 702).

By neutralising an aqueous solution of hydroferricyanic acid with baryta-water, and dissolving the barium ferricyanide in water, together with some bromine, the author obtained a solution which on evaporation yielded crystals of the compound $Ba_3Fe_2Cy_{12} + 2BaBr_2 + 20H_2O$.

The yellow precipitate formed by an excess of potassium ferricyanide in a solution of a silver salt, is free from potassium, and is not decomposed by dilute nitric acid. A. G. B.

Derivatives of Potassium Platinocyanide. By T. WILM (*Ber.*, **22**, 1542—1546; compare Abstr., 1888, 931).—When the chlorine-derivative previously described (*loc. cit.*) is digested with warm aqueous ammonia, a compound, $Pt(CN)_4,2NH_3$, is produced. This forms heavy, white, rhombic plates, soluble in boiling water, insoluble in alcohol. The same compound is obtained by the action of warm ammonia on the perchloride of the cyanide. When cold ammonia is used, the compound is mixed with another yellow substance, which is probably an intermediate compound of the formula $KCN,Pt(CN)_3,NH_3$. The filtrate from these compounds when evaporated, left a yellow crystalline mass, which on exposure to the air in a moist state, became gradually converted into the original copper-red crystals. Fresh analysis of the chlorine compound led to the formula $3[2KCN,Pt(CN)_2,3H_2O]Cl + 2H_2O$. Attempts to determine the molecular weight by Raoult's method proved unsuccessful.

L. T. T.

The Discovery of the Normal Tricyanides. By R. OTTO (*Ber.*, **22**, 1446—1447).—A claim of priority.

Synthesis of Cyanphenin. By F. KRAFFT (*Ber.*, **22**, 1759—1760).—A reply to Otto (preceding, *Ber.*, **22**, 1446).

Derivatives of Cyanamide. By A. SMOLKA and A. FRIEDREICH (*Monatsh.*, **10**, 86—100).—Biguanide (guanylguanidine) may be conveniently prepared (compare Abstr., 1888, 830) by heating a mixture of dicyanodiamide with an ammonium salt.

Dicyanodiamidine (guanyl carbamide), $NH_2{\cdot}C(NH){\cdot}NH{\cdot}CONH_2$, is formed by digesting silver amidodicyanate with ammonium chloride solution at 130—140°; by heating together for two days solutions of carbamide and cyamide; or by heating at 150—160° a mixture of cyanuric acid and guanidine carbonate.

Melamine is formed in the decomposition of guanidine salts by heat; or by heating them with dicyanodiamide.

Ammeline is obtained by heating salts of biguanide with carbamide.

Melanuric acid (ammelide) may be prepared by heating guanidine carbonate with excess of carbamide, whereby the dicyanodiamine first formed reacts with the excess of carbamide.

Biuret dicyanodiamide is formed by continued heating of a mixture of guanidine carbonate and carbamide in molecular proportion; dicyanodiamidine is first formed, and then decomposes into ammonia and biuret dicyanodiamide. G. T. M.

Bromotrimethyl Carbinol. By L. GARZINO (*Chem. Centr.*, 1889, 571, from *Ann. Chim. Farm.*, **9**, 96—99).—*Bromotrimethyl carbinol*,

$CH_2Br{\cdot}CMe_2{\cdot}OH$, prepared from dibromótrimethylmethane by boiling with water, boils at 136—138° with decomposition, and cannot even be distilled in a vacuum without partial decomposition. It is very soluble in ether, somewhat soluble in water. When 5 grams of the carbinol is boiled for four hours with 25 c.c. of a saturated solution of ammonium sulphate, and subsequently treated with baryta-water, &c., the *sodium* parahydroxyisobutylenemonosulphonate is obtained, which is identical with that already (Abstr., 1887, 436) prepared from isobutylene bromide. By heating 5 grams of monobromotrimethyl carbinol with 3·3 grams triethylamine, triethylamine hydrobromide is obtained. It is soluble in alcohol, insoluble in ether, readily soluble in water, and melts at 248—250° with decomposition. Trimethylamine hydrobromide may be prepared in a similar manner.

Monobromotrimethyl carbinol injected into a guinea-pig caused excitement, primarily followed by an almost complete paralysis of the hinder extremities, and finally general prostration. The effects disappeared at the end of two hours. Similar effects were observed with a rabbit. J. W. L.

Pentacetyldextrose. By E. Erwig and W. Koenigs (*Ber.*, **22**, 1464—1467).—*Pentacetyldextrose*, $C_6H_7O(OAc)_5$, is formed when pure grape-sugar (5 grams) is added to hot acetic anhydride (20—22 c.c.) containing a small quantity of zinc chloride, and the mixture boiled for about 10 minutes to complete the reaction. The solution is evaporated to dryness, the residue evaporated twice with alcohol to free it from acetic acid, then crystallised from a little hot alcohol, washed with cold water, and finally repeatedly recrystallised from boiling absolute alcohol with addition of animal charcoal. The yield is 60 per cent. of the sugar employed. Pentacetyldextrose can also be obtained by boiling pure octacetyldiglucose for half an hour with acetic anhydride and a trace of zinc chloride. It crystallises in slender, colourless needles, melts at 111—112°, and is readily soluble in ether, chloroform, benzene, and glacial acetic acid, but only sparingly in water, carbon bisulphide, and light petroleum. It has a slightly bitter taste, reduces Fehling's solution when boiled therewith, and in chloroform solution is strongly dextrorotatory. It does not give the aldehyde reaction with magenta-sulphurous acid solution, and it is only very slowly acted on by a warm alcoholic solution of phenylhydrazine. It is not acted on by phosphoric chloride in boiling chloroform solution, but when heated with the chloride alone at 110—112°, a reaction takes place. The formation of pentacetyldextrose can be employed for the identification of grape-sugar.

F. S. K.

Oxidation of Rhamnose (Isodulcitol). By W. Will and C. Peters (*Ber.*, **22**, 1697—1704; compare Abstr., 1888, 933).—Malin (*Annalen*, **145**, 197) states that by the oxidation of rhamnose with nitric acid an acid, $C_6H_{10}O_9$, is formed. The authors have repeated this work, but find that in every case trihydroxyglutaric acid (Kiliani, this vol., p. 32) is formed. This result agrees with the view that rhamnose is a methylarabinose, the separation of a methyl-group during the oxidation having many analogies with similar compounds.

The lactone, $C_6H_{10}O_5$, previously described (Abstr., 1888, 933) was carefully crystallised, when rhombic crystals were obtained, giving the axial ratios $a : b : c = 0·6873 : 1 : 1·2600$. This lactone is, therefore, not identical with Haushofer's metasaccharin. L. T. T.

Melitose (Raffinose). By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **22**, 1678—1686).—The results already obtained by various workers in the inversion of melitose appear to indicate that the C_{18} molecule is not at once broken up into three C_6 molecules, but first into a C_{12} and a C_6 molecule. By very careful inversion with very dilute sulphuric acid, the authors have succeeded in confining the inversion to the first stage. 1 gram of melitose was dissolved in water, 0·6 c.c. sulphuric acid of sp. gr. 1·0594 added, the whole diluted to 10 c.c., and heated for one hour. The sulphuric acid was then removed with barium carbonate, and phenylhydrazine and acetic acid added. Of the ozasone formed, part was soluble in boiling water, and was, therefore, formed from a disaccharide, and part insoluble. The insoluble osazone showed all the properties of phenylglucosazone. That the sugar contained therein is levulose is proved by the great reduction of the dextro-rotation of melitose by the partial inversion, and also by the fact that if the product of inversion be evaporated to the consistency of syrup and extracted with ether-alcohol, a levorotatory sugar is obtained in solution. The part of the residue insoluble in ether-alcohol yields an osazone, soluble in boiling water, which analysis showed to have the constitution $C_{24}H_{32}N_4O_9$, and, therefore, to be the osazone of a disaccharide. The mixture of two-thirds disaccharide and one-third levulose has a rotation of $[\alpha]_D = 50°$,* and that of the disaccharide is probably higher than that of melitose. This disaccharide is, therefore, not lactobiose (lactose), which it closely resembles, but a new carbohydrate, for which the author proposes the name *melibiose*. The evaporated product of the inversion, when extracted with ether-alcohol, leaves this melibiose as a residue, but the authors have not yet obtained this in a crystalline or pure form.

When melitose is fully inverted, which is effected, though with partial further decomposition, by mixing 1 gram melitose with $1\frac{1}{2}$ c.c. sulphuric acid of sp. gr. 1·0567, diluting to 10 c.c., and boiling for $6\frac{1}{2}$ hours, the product consists of 1 mol. galactose and 2 mols. levulose, or 1 mol. levulose and 1 mol. dextrose.

The author recommends the name *melitriose* for this carbohydrate, as retaining, to a great extent, the older name melitose, showing that it has a C_{18} molecule, and doing away with the name raffinose, which was based on the misapprehension that the compound was formed during the refining of the sugar. L. T. T.

Diisopropylamine. By K. H. M. VAN DER ZANDE (*Rec. Trav. Chim.*, 8, 202—214).—Unsuccessful attempts were made to obtain this substance from crude isopropylcarbamide, made from isopropyl iodide and silver cyanide, and containing excess of the iodide.

Finally, Hofmann's method was adopted, and isopropyl iodide was heated at 100° for 4½ hours in a sealed tube with a 27·5 per cent. aqueous or 15 per cent. alcoholic solution of ammonia, the latter being preferred. Some propylene was always formed, and in an alcoholic solution some ethyl isopropyl ether also. The contents of the tube were evaporated, and the residue distilled with potash; the distillate boiled at 30—85°, and hence contained much primary amine. More isopropyl iodide was added; after warming for a quarter of an hour, the contents of the tube solidified. The crystalline mass was dissolved in water and treated with potash, the mixture of amines thus obtained boiled at 67—85°. It was neutralised with hydrochloric acid and a concentrated solution of sodium nitrite added; much gas was evolved, and a crystalline substance was deposited in considerable quantity. This substance is easily soluble in water, hence, in preparing it as described above, the solution must be kept concentrated. It was recrystallised from benzene, when it melted at 138°, or better from ethyl acetate, when it melted at 140°; analysis showed that it was *diisopropylammonium nitrite*, $NH_2Pr^{\beta}\cdot NO_2$. When boiled with water it decomposes slowly, giving *diisopropylnitrosamine*, $NPr_2^{\beta}\cdot NO$, a very volatile substance, melting at 46°, and boiling at 194·5°. Diisopropylamine can be prepared from the nitrite by treatment with potash, but it was obtained purer by boiling the nitrosamine with hydrochloric acid, evaporating the excess of the acid, and distilling the residue with potash; thus obtained it boils at 83—84° at 752 mm. It has a more ammoniacal odour than the normal diamine, and, unlike the latter, mixes with water in all proportions; its most remarkable property is the formation of a stable compound with nitrous acid.

This is not the only peculiarity of diisopropylamine-derivatives; the unsymmetrical carbamide cannot be made in the usual way, and van Romburgh finds that the amine itself, when treated with an alcoholic solution of picryl chloride, does not give a substituted picramide, but ethyl picrate, boiling at 78·5°. C. F. B.

Action of Ethyl Iodide and Zinc on Paraldehyde. By W. Wwedensky (*J. pr. Chem.* [2], 39, 538—541).—A mixture of paraldehyde and ethyl iodide, in the proportions of 1 mol. of the former to 2 of the latter, was poured on recently ignited, finely-granulated zinc, allowed to remain for two days, and then heated for two or three days until the mass became solid. The product thus obtained was decomposed with water; gas was evolved and zinc oxide precipitated; sulphuric acid was then added to dissolve the latter, and the whole distilled. A third of the distillate thus obtained was again distilled over and treated with potash; an oil was obtained, distilling between 70° and 80°, which, when treated with hydriodic acid, gave nothing but ethyl iodide. In a second experiment, the same mixture was allowed to remain at the atmospheric temperature during the three summer months, and then treated as described above. The distillate was fractionated into two parts, one distilling between 72° and 74°, found by analysis to consist of ethyl iodide; the other distilling between 118° and 120° and consisting of butyl iodide; the first fraction was about three times as large as the second. This butyl iodide was treated with lead oxide and water, and a small quantity of an alcohol distilling between 95° and 100° was obtained. This was oxidised with chromic mixture, and on distillation gave nothing but acetic acid. At the commencement of the distillation, a slight odour, as of a ketone—doubtless methyl ethyl ketone—was also observed. The author concludes that if any secondary butyl alcohol is formed in the reaction described, the quantity is so small that it must be derived from acetaldehyde, which is unavoidably formed from paraldehyde under the conditions of the reaction; and consequently that zinc and ethyl iodide have no action on paraldehyde itself. It had already been shown that neither zinc-ethyl nor a mixture of allyl iodide and zinc has any action on paraldehyde. C. F. B.

Symmetrical Tetrachloracetone. By T. ZINCKE and O. KEGEL (*Ber.*, 22, 1478—1482; compare Levy and Jedlicka, Abstr., 1888, 443).—A yellow, crystalline compound, $C_{15}H_{12}N_4$, melting at 126°, is obtained when tetrachloracetone is treated with phenylhydrazine in acetic acid solution. This substance is identical with the compound (m. p. 122°) prepared by Pechmann and Wehsarg (this vol., p. 34) by treating dinitrosoacetone with phenylhydrazine. When warmed with stannous chloride and concentrated hydrochloric acid, it yields considerable quantities of aniline, but the largest portion is converted into two other basic compounds. One of these bases forms a *hydrochloride*, $C_{15}H_{14}N_4,HCl$, which is only sparingly soluble in the cold, and separates from the solution in colourless plates, readily soluble in hot water. The *sulphate*, $(C_{15}H_{14}N_4)_2,H_2SO_4$, is much more sparingly soluble in water, and crystallises in thin, colourless plates. The free *base* crystallises from light petroleum in small, colourless plates, melts at 75—77°, and turns dark-green on exposure to light. The other *base*, $C_{15}H_{14}N_4$, is obtained, together with aniline, when the filtrate from the preceding compound is treated with hydrogen sulphide, the filtered solution evaporated, and the residue dissolved in water, and carefully decomposed with sodium carbonate. It crystallises in colourless, rhombic plates, melts at 192—193°, and turns reddish on keeping. The *hydrochloride* and the sulphate are readily soluble. F. S. K.

Preparation of Concentrated Formic Acid. By MAQUENNE (*Bull. Soc. Chim.*, 50, 662—664).—A mixture of crystalline formic acid and the glacial monohydrate of sulphuric acid does not evolve carbon monoxide until heated to 60°. The author makes use of this observation and of the fact that under reduced pressure formic acid may be made to boil at temperatures below 60°, to concentrate aqueous formic acid. The only precautions necessary are that the sulphuric acid should be added in quantity less than sufficient to form with the water present in the aqueous solution the hydrate H_2SO_4,H_2O, and that the distillation take place below 75°.

When commercial formic acid containing 45—50 per cent. of water is treated with an equal weight of sulphuric acid and distilled under reduced pressure at 66°, a distillate containing 84—85 per cent. of real formic acid is obtained, and this distillate when distilled under reduced pressure at 65° with one-half its weight of sulphuric acid will yield a solution containing 98 per cent. of real formic acid. The loss is small. T. G. N.

Drying Oils. By K. Hazura (*Monatsh.*, **10**, 190—195; compare Abstr., 1887, 357, 799, 913; and 1888, 816, 817, 1270).—The author has examined pure sunflower oil, obtained from the firm of Röder, of Vienna, and finds it has an iodine number 134·5, and a saponification number 191·6. The liquid fatty acids contained in it are shown by their behaviour on oxidation and bromination to consist almost entirely of linoleïc acid, $C_{18}H_{32}O_2$, mixed with a small quantity of oleïc acid. G. T. M.

Oxidation of Unsaturated Fatty Acids. By A. Grüssner and K. Hazura (*Monatsh.*, **10**, 196—199; compare Abstr., 1888, 1270).—Brassic and ricinelaidic acids, on oxidation with alkaline potassium permanganate, behave in conformity with the rule laid down by Hazura. The former is converted into *isodihydroxybehenic acid*, $C_{21}H_{41}(OH)_2{\cdot}COOH$, which is insoluble in water and light petroleum, dissolves readily in hot alcohol and acetic acid, and crystallises from a dilute alcoholic solution in microscopic rhombic plates melting at 98—99°; the latter into *β-isotrihydroxystearic acid*,

$$C_{17}H_{32}(OH)_3{\cdot}COOH,$$

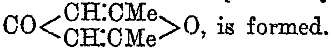
which is insoluble in cold water, crystallises from hot benzene in short, rhombic prisms, and from dilute alcohol in gleaming scales which melt at 114—115°. G. T. M.

Derivatives of Myristic Acid. By C. Hell and S. Twerdomedoff (*Ber.*, **22**, 1745—1748).—*Bromomyristic acid*, $C_{14}H_{27}BrO_2$, is easily obtained by gradually adding bromine (1 mol.) to an intimate mixture of myristic acid (1 mol.) and a little amorphous phosphorus, and then heating for 3—4 hours on the water-bath. The product is repeatedly washed with hot water, cooled, pressed between paper, and recrystallised from benzene or alcohol. It crystallises in colourless, waxy, microscopic needles, melts at 31°, and is soluble in all ordinary solvents except water.

Hydroxymyristic acid is prepared by boiling the bromo-derivative with excess of soda for 20—24 hours and decomposing the resulting sparingly soluble sodium salt with dilute sulphuric acid. When the acid is boiled with water, it becomes almost solid and opaque, but on cooling it liquefies and becomes more transparent. It crystallises from ether or benzene, melts at 51—51·5°, and is insoluble in hot or cold water, but is readily soluble in other solvents. This acid seems to be identical with the compound obtained by Müller (Abstr., 1882, 496) from the ethereal oil of the fruit of *angelica archangelica*. The *barium* salt, $(C_{14}H_{27}O_3)_2Ba$, is more readily soluble in cold than in hot water. The *silver* salt, $C_{14}H_{27}O_3Ag$, prepared by precipitating a hot, alcoholic solution of the acid with silver nitrate, is colourless, but blackens on exposure to light.

Amidomyristic acid, $C_{14}H_{27}O_2{\cdot}NH_2$, prepared by heating bromomyristic acid with hot alcoholic ammonia for 5—6 hours at 100°, and crystallising the product from hot glacial acetic acid, is a colourless, crystalline powder, melts at 253°, and is insoluble in alcohol, ether, benzene, light petroleum, and dilute acids.

Anilidomyristic acid, $C_{14}H_{27}O_2\cdot NHPh$, prepared in like manner, separates from hot alcohol in colourless crystals, melts at 143°, and is readily soluble in hot ether and alcohol, but only sparingly in benzene, and insoluble in water. It dissolves in warm alkalis and ammonia, but is insoluble in concentrated hydrochloric acid. In hot alcoholic solutions copper acetate produces a dark-green, and magnesium salts a colourless, precipitate. F. S. K.

Dehydracetic Acid. By F. Feist (*Ber.*, **22**, 1570—1571).—When dehydracetic acid is heated with acids, preferably with hydriodic acid, *dimethylpyrone*,  $CO<\genfrac{}{}{0pt}{}{CH:CMe}{CH:CMe}>O$, is formed. This substance forms glistening crystals, soluble in ether, melting at 132°, and boiling at 248—249° under 719 mm. pressure. It sublimes slowly at 80° in long needles, very soluble in water. When an aqueous solution of this dimethylpyrone is boiled with baryta, a yellow xantho-salt, $C_7H_8O_3Ba + 4H_2O$, is formed, which when treated with acids yields a *triketone*, $COMe\cdot CH_2\cdot CO\cdot CH_2\cdot COMe$, which crystallises in large scales, and melts at 49°. At a higher temperature, it gives off water and is reconverted into dimethylpyrone. The triketone when heated with ammonia is converted almost quantitatively into lutidone, obtained by Haitinger by the action of ammonia on dehydracetic acid. The author was unable to obtain lutidone direct from dimethylpyrone. L. T. T.

Synthesis of Ketone Acids by the Action of Acid Chlorides on Propionitrile in Presence of Aluminium Chloride. By R. Otto and J. Tröger (*Ber.*, **22**, 1455—1456).—*α-Propionylpropionamide*, $COEt\cdot CHMe\cdot CONH_2$, is obtained by gradually adding aluminium chloride to a mixture of propionitrile and propionic chloride, warming for a short time on the water-bath to complete the reaction, and carefully decomposing the product with water. It crystallises from dilute alcohol in small needles, sublimes below 100°, melts at 152—153°, and is only sparingly soluble in cold water, but readily in hot water, alcohol, and ether. It forms a crystalline compound with mercuric oxide, and is readily decomposed by cold potash with evolution of ammonia. When warmed with dilute sulphuric acid, it is decomposed into ammonia and propionic acid. F. S. K.

Manganese Oxalate. By J. Castelaz (*Bull. Soc. Chem.*, **50**, 645—647).—This substance, which is largely used as an oil siccative, cannot be obtained in a satisfactory manner by acting on manganese chloride or sulphate with sodium or potassium oxalate, as under these conditions double salts are invariably formed, which remain in the mother-liquors. The author proposes to prepare the salt by acting on moist manganese carbonate free from iron and calcium salts, with a solution of oxalic acid. 2 to 5 per cent. of manganese oxalate suffice to render oils drying, and when the mixture thus prepared is heated at 150°, decomposition of the oxalate ensues, with evolution of carbonic oxide and carbonic anhydride. T. G. N.

Action of Phosphorus Pentachloride on Malonic Acid. By A. Béhal and V. Auger (*Bull Soc. Chim.*, **50**, 631—635).—When malonic acid acts on excess of phosphorus pentachloride, and the resulting product is distilled under reduced pressure, malonic chloride mixed with phosphorus oxychloride is obtained. If only the theoretical quantity of pentachloride is used, a crystallisable residue is left after distillation, from which absolute ether extracts a compound of the formula $C_9H_5ClO_6$, crystallising from carbon bisulphide in long needles melting at 122°. The residue also contains a substance less soluble in carbon bisulphide, from which it crystallises in warty masses. T. G. N.

Barium Malonates. By Massol (*Compt. rend.*, **109**, 27—29).—Heat of neutralisation of malonic acid by barium oxide: first equivalent = $+13.495$ Cal.; second equivalent, with partial precipitation of the normal salt = $+16.64$ Cal.

Solutions containing the acid and base in the proportion required to form hydrogen barium malonate yield only the normal salt when concentrated.

When malonic acid is mixed with the proper proportion of a solution of barium hydroxide, a bulky, flocculent precipitate separates, and gradually becomes crystalline. It forms long, slender needles, containing 2 mols. H_2O, and is very slightly soluble in water. At 100° it loses half its water, and forms the salt which Finkelstein obtained by crystallisation from boiling solutions. The monohydrated salt crystallises in short, brilliant, white prisms, which retain their water at 140° under ordinary conditions, but become anhydrous at this temperature in a current of hydrogen.

Heat of dissolution: dihydrate = -3.83 Cal.; monohydrate = -1.92 Cal.; anhydrous = $+3.48$ Cal.

$C_3H_4O_4$ solid + $Ba(OH)_2$ solid = $C_3H_2O_4Ba$ solid + $2H_2O$ solid .... develops $+31.83$ Cal.

This value is intermediate between that for the acetate and that for the oxalate.

$BaC_3H_2O_4$ solid + $2H_2O$ solid = $BaC_3H_2O_4,2H_2O$ solid develops $+7.38$ Cal.

$BaC_3H_2O_4$ solid + H_2O solid = $BaC_3H_2O_4,H_2O$ solid ,, $+6.90$ Cal.

C. H. B.

Action of Ethyl Iodide and Zinc on Ethyl Malonate. By S. Joulowsky (*J. pr. Chem.* [2], **39**, 446—451).—Ethyl malonate (20 grams) was mixed with ethyl iodide (100 grams) and granulated zinc in a reflux apparatus which was heated over a water-bath. When gas (probably ethane) ceased to be evolved, water was added and the mixture distilled. The oily distillate was dried over potash and fractionated. The fraction 219—221° was largest, and proved to be ethyl diethylmalonate (Conrad, Abstr., 1879, 707). The acid sodium and potassium salts of *diethylmalonic acid* were obtained.

A. G. B.

Formation of Dimethylsuccinic Acid. By C. HELL and M. ROTHBERG (*Ber.*, **22**, 1737—1742).—Dimethylsuccinic acid can be obtained by treating isobutylene bromide with potassium cyanide and hydrolysing the resulting cyanide with hydrochloric acid. In preparing large quantities of isobutylene by Lermontoff's method (*Annalen*, **196**, 107), it is unadvisable to add fresh quantities of isobutyl alcohol and sulphuric acid to the exhausted mixture, but to employ fresh sand for each operation; the yield is also better when the mixture is left for some time with sand at the ordinary temperature and then heated gently. The bromide is obtained by passing the gases through a condenser, collecting the less volatile products, amongst which is acetone, in a receiver, and absorbing the isobutylene, after washing with soda, in a series of bulbs containing bromine.

Isobutylene cyanide (dimethylsuccinonitrile), $CN{\cdot}CMe_2{\cdot}CH_2{\cdot}CN$, is best prepared from the bromide by treating the latter with an aqueous alcoholic solution of potassium cyanide containing a little hydrogen cyanide, and keeping the mixture at the ordinary temperature for two weeks. The filtered solution is evaporated, the residue treated with water, the nitrile extracted with ether, and fractionated. The yield is very small. It is a colourless oil, boils at 218—220°, and is moderately easily soluble in water. When heated at 150° with concentrated hydrochloric acid, it is decomposed into ammonia and dimethylsuccinic acid, melting at 137—138°. The acid is converted into the anhydride when heated at 165—170°.

The dimethylsuccinic acid (m. p. 74°) described by Tate, and obtained by treating ethyl α-bromisobutyrate with ethyl sodoacetoacetate, is probably hydroxybutyric acid.

F. S. K.

Disubstituted Succinic Acids. By C. A. BISCHOFF and P. WALDEN (*Ber.*, **22**, 1812—1818 and 1819—1822; compare Abstr., 1888, 254, 1057; this vol., p. 490).—Owing to the discrepant statements on the subject, the authors have determined the melting points of the isomeric tartaric acids, and find that dextro- and levotartaric acid begin to fuse at about 168° and are completely melted at about 170°, that racemic acid begins to fuse at about 204° and is completely melted at about 206°, and that antitartaric (mesotartaric) acid begins to fuse at about 140° and is completely melted at about 143°.

Ethyl methylbutenyltricarboxylate, obtained by methylating ethyl butenyltricarboxylate, boils at 270° with slight decomposition and has a density of 1·0903 at 15°. On hydrolysis, it yields symmetrical *ethylmethylsuccinic acid* which melts at 168 5°.

Ethyl benzylbutenyltricarboxylate boils at 248° under a pressure of 45 mm., and has a density of 1·0825 at 19°. On hydrolysis with alcoholic potash, it yields symmetrical *benzylethylsuccinic acid*, which melts at 153—155°.

The results of experiments on the conductivity of solutions of the alkyl succinic acids are given in the paper. It is also stated that the para- and the anti-symmetrical diethylsuccinic acids cannot be split into optically active isomerides by the *Penicillium* method, being obtained unchanged at the end of every experiment. W. P. W.

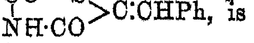
Thiosuccinic Anhydride. By C. U. ZANETTI (*Chem. Centr.*, 1889, 668, from *Rend. Acad. dei Lincei* [4], **5**, i, 225—227).—When thiosuccinic anhydride is heated with bromine for several hours at 108—110°, it forms a greenish-brown oil which solidifies to a crystalline mass after some time. Thiosuccinic anhydride combines with 2 mols. of aniline and of phenylhydrazine, irrespective of the proportions of the two substances present together.

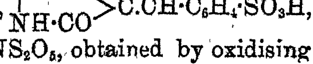
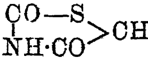
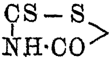
Succinylodiphenylhydrazine, $C_2H_4(CO{\cdot}NH{\cdot}NHPh)_2$, is prepared by mixing the anhydride and hydrazine in 90 per cent. acetic acid, precipitation with water, and repeated recrystallisation from boiling alcohol. It melts at 219°, is insoluble in cold water, alcohol, benzene, and chloroform, and is but sparingly soluble in these liquids when hot. It decomposes a few degrees above its melting point. Concentrated nitric acid decomposes it; in concentrated sulphuric acid it dissolves with a transient purple-red coloration; it dissolves in hot potash without decomposition. It may also be prepared directly from succinic anhydride by the action of phenylhydrazine. J. W. L.

Thiocarbimidacetic and Rhodanic Acid. By R. ANDREASCH (*Monatsh.*, **10**, 73—81; compare *Ber.*, **17**, 2277).—Thiocarbimidacetic acid resembles rhodanic acid in forming a condensation product with benzaldehyd. The operation is best conducted by placing together finely powdered thiocarbimidacetic acid (1 mol.)—slightly more than the theoretically calculated quantity of benzaldehyd—and caustic soda (1 mol.) in a little water containing sufficient alcohol to just dissolve the oily aldehyde. After a time, the *sodium* salt of *carbaminesulphydrylcinnamic acid* (*benzylidenecarbaminethioglycolic acid*,

$$NH_2{\cdot}CO{\cdot}S{\cdot}C(COONa){:}CHPh + 1\tfrac{1}{2}H_2O,$$

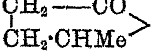
crystallises in thin scales, which melt with decomposition at 160° and are only slightly soluble in cold water and cold alcohol.

Benzylidenecarbimidoacetic acid,  $\begin{matrix}CO-S\\ |\\ NH{\cdot}CO\end{matrix}\!\!>C{:}CHPh$, is precipitated on adding hydrochloric acid to the warm aqueous solution of the above-mentioned sodium salt. It crystallises from alcohol in thin scales, melts at 242°, and contains a molecule of water less than the acid corresponding to the sodium salt above described.

Carbaminesulphydrylcinnamic acid is converted, by long heating at 150° with four times its weight of concentrated sulphuric acid, into sulphobenzylidenethiocarbimidacetic acid,  $\begin{matrix}CO-S\\ |\\ NH{\cdot}CO\end{matrix}\!\!>C{:}CH{\cdot}C_6H_4{\cdot}SO_3H$, which is identical with the acid $C_{10}H_7NS_2O_5$, obtained by oxidising benzylidenerhodanic acid (Ginsburg and Bondzynski, Abstr., 1886, 325). From this identity it appears that benzylidenethiocarbimidacetic acid and benzylidenerhodanic acid have constitutions analogous to thiocarbimidacetic acid,  $\begin{array}{l}\mathrm{CO{-}S}\\ \mid \\ \mathrm{NH{\cdot}CO}\end{array}\!\!>\mathrm{CH_2}$, and rhodanic acid,  $\begin{array}{l}\mathrm{CS-S}\\ \mid \\ \mathrm{NH{\cdot}CO}\end{array}\!\!>\mathrm{CH_2}$, respectively. G. T. M.

New Synthesis of Rhodanic Acid. By J. Freydl (*Monatsh.*, **10**, 82—85).—The author has synthesised rhodanic acid by treating thioglycolic acid (obtained from potassium sulphydrate and chloracetic acid) dissolved in absolute alcohol, with excess of potassium thiocyanate, and saturating the mixture with hydrogen chloride. The strongly smelling product was evaporated over a water-bath, separated from an oily substance (thioglycollic ether?) and allowed to cool, when the acid separated; on recrystallisation from water it melted at 168° and gave all the reactions of rhodanic acid as described by v. Nencki. G. T. M.

γ-Amidovaleric Acid. By J. Tafel (*Ber.*, **22**, 1860—1865: compare Abstr., 1886, 1008).—γ-Amidovaleric acid is best obtained by boiling the anhydride (see below) with baryta, saturating the hot solution with carbonic anhydride, evaporating the filtrate and treating the residual acid with alcohol to hasten crystallisation. 10 grams of the anhydride yield 10·3 grams of the crystalline acid. The potassium salt and the sodium salt are amorphous, deliquescent compounds, having a strongly alkaline reaction and are soluble in alcohol; all the salts with bases are decomposed by carbonic anhydride. The *hydrochloride*, $C_5H_{11}NO_2,HCl$, prepared by precipitating an alcoholic hydrochloric acid solution of the acid with ether, is a crystalline compound, melts at 154°, and is readily soluble in water and alcohol. The *platinochloride* crystallises in bright-yellow plates, decomposes at about 200°, and is readily soluble in water but rather sparingly in hot alcohol. *Ethyl amidovalerate hydrochloride*, $C_7H_{15}NO_2,HCl$, can be prepared by passing hydrogen chloride into a boiling alcoholic solution of the acid. It crystallises from alcoholic ether in plates, melts at 92°, and is very readily soluble in water and alcohol; it is not acted on by an aqueous solution of sodium nitrite in the cold, but on warming a rapid evolution of gas commences.

Methylpyrrolidone,  $\begin{array}{l}\mathrm{CH_2{-}{-}CO}\\ \mid \\ \mathrm{CH_2{\cdot}CHMe}\end{array}\!\!>\mathrm{NH}$ (γ-amidovaleric anhydride), is best prepared as follows:—The alcoholic solution of the reduction product of levulinic acid hydrozone (*loc. cit.*) is neutralised with soda, heated at 130° to free it from alcohol, the liquid decanted, and the crystalline mass which is obtained on cooling agitated with ether to remove the aniline. The whole is then carefully heated at 280° for 2—3 hours in a copper retort. Most of the methylpyrrolidone remains in the residue and is isolated by repeatedly extracting with ether; the small quantity contained in the portion of the distillate passing over above 160° is isolated by saturating with potassium carbonate and extracting the separated oil with ether. The ethereal solutions are mixed together, and after evaporating the ether the residual brown oil is fractionated. Water and a basic compound—probably methylpyrrolidine—distil first, afterwards methylpyrrolidone collects in the receiver and is purified by redistilling under reduced pressure. The yield is about 25 per cent. of the hydrazone employed. It is a yellowish oil, solidifies in a freezing mixture to colourless crystals melting at 37°, and does not give any of the ordinary pyrroline reactions. The *hydrochloride*, C_5H_9NO,HCl, crystallises in colourless needles, melts at 110°, and is readily soluble in alcohol and water. The *platinochloride*, $(C_5H_9NO)_2,H_2PtCl_6 + 2C_5H_9NO$, is a yellowish crystalline compound. The *nitrosamine*, $C_5H_8N_2O_2$, is formed when a concentrated solution of sodium nitrite (7·5 parts) is slowly added to a well-cooled solution of methylpyrrolidone (10 parts) in water (30 parts) and concentrated hydrochloric acid (20 parts). It separates as a yellow oil when the well-cooled solution is saturated with potassium carbonate. It gives Liebermann's reaction, and when distilled under diminished pressure it yields valerolactone, methylpyrrolidone and tarry products. Sodium γ-hydroxyvalerate is formed when a hydrochloric acid solution of the nitrosamine is treated with soda in the cold; this sodium salt is decomposed by boiling dilute sulphuric acid, yielding valerolactone and small quantities of methylpyrrolidone.

F. S. K.

Oxamic Acid. By L. Oelkers (*Ber.*, **22**, 1566—1569).—The author has carefully re-examined this substance. It is best prepared by heating an aqueous solution of oxamethane to boiling and gradually adding ammonia until the liquid becomes alkaline. The solution of the ammonium salt produced should be concentrated and hydrochloric acid added. Oxamic acid then crystallises out on cooling. It forms a white, crystalline powder melting at 210°. The melting point 173° given in the text-books is probably due to the presence of impurities.

L. T. T.

Unsymmetrical Dialkylcarbamides. By K. H. M. van der Zande (*Rec. Trav. Chim.*, **8**, 222—247).—Dimethyl-, diethyl-, dipropyl-, and diisopropyl-carbamides were prepared by Wöhler's method, by evaporating an aqueous solution containing equivalent quantities of the sulphate of the amine, and of potassium isocyanate. In the first three cases, the yield was nearly theoretical, but in the last only 15 per cent. of the theoretical, as diisopropyl isocyanate was found to decompose into the amine, ammonia, and carbonic anhydride. These substituted carbamides are all very soluble; they form compounds with oxalic and picric acids, and sometimes with nitric acid, their reactions with acetic anhydride, aldehyde, chloral, and œnanthol were also studied.

Dimethylcarbamide, $NH_2\cdot CO\cdot NMe_2$, was prepared, and shown by Raoult's method to have the simple formula given above. Its compound with oxalic acid, $C_3H_8N_2O,C_2H_2O_4 + H_2O$, decomposes at 105°; that with picric acid, $C_3H_8N_2O,C_6H_3N_3O_7$, melts with decomposition at 130°.

Diethylcarbamide, $NH_2\cdot CO\cdot NEt_2$, melts at 74°, and was shown by

Raoult's method to have the above simple formula. The oxalate, $2C_5H_{12}N_2O,C_2H_2O_4$, decomposes at 122°, the picrate,

$$C_5H_{12}N_2O,C_6H_3N_2O_7,$$

melts with decomposition at 135°.

Dipropylcarbamide, $NH_2{\cdot}CO{\cdot}NPr^{\alpha}{}_2$, melts at 76°, its oxalate, $2C_7H_{16}N_2O,C_2H_2O_4$, melts at 103°; its picrate, $C_7H_{16}N_2O,C_6H_3N_3O_7$, melts at 135°. A nitrate, $C_7H_{16}N_2O,2HNO_3$, was also prepared.

Diisopropylcarbamide, $NH_2{\cdot}CO{\cdot}NPr^{\alpha}{}_2$, melts at 103°; its oxalate, $2C_7H_{16}N_2O,C_2H_2O_4$, decomposes at 111°; the picrate melts at 134°; and the nitrate, $C_7H_{16}N_2O,HNO_3$, melts at 79°.

When dimethylcarbamide was boiled with acetic anhydride, isocyanuric acid was deposited, and the liquid yielded large quantities of dimethylacetamide, but acetic acid was not formed. The same reaction took place with the other three carbamides.

Dimethylcarbamide when allowed to remain for two days with acetaldehyde yields the compound $CH_3{\cdot}CH(NH{\cdot}CO{\cdot}NMe_2)_2$, which melts at 160°. This reaction does not occur in alcoholic solution, nor does diethylcarbamide behave in like manner, but in ethereal solution with aldehyde this substance gives an ethyl compound analogous to the methyl one, and melting at 144°. Similar compounds were also obtained with dipropyl- and diisopropyl-carbamides; these melt at 113° and 147° respectively. These compounds are decomposed by boiling with dilute acids or alkalis, but not with water.

Chloral and dimethyl-carbamide in concentrated aqueous solution gave (1) small crystals melting at 156°, of the formula

$$CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NMe_2.$$

which may be regarded as an additive compound of chloral; and (2) large crystals melting at 74°, and easily changing to (1); these have the formula $C_3H_8N_2O,C_2H_3Cl_3O_2$, an additive compound of chloral hydrate. Diethylcarbamide gives only an additive compound with chloral, melting at 142°. Dipropylcarbamide gives a similar compound melting at 128°, and also a chloral hydrate additive compound melting at 51°. Diisopropylcarbamide gives only a chloral additive product, which melts at 121°. These compounds are decomposed by boiling with dilute acids and alkalis, but not by boiling with water.

Œnanthaldehyde was allowed to remain for a few days with dimethylcarbamide, the product melted at 139—140°, or when crystallised from ether at 180° (?); but it decomposed rapidly, and no satisfactory analysis could be carried out. With diethylcarbamide, better results were obtained; the product melted at 95°, and had the formula $C_7H_{14}(NH{\cdot}CO{\cdot}NEt_2)_2$. Dipropylcarbamide gave an analogous substance melting at 113°.

Attempts to prepare compounds with benzaldehyde and with ketonic compounds were not successful.

In conclusion, the author adduces reasons for regarding these carbamides as substituted amides of amidoformic acid; he thinks they react more like amic acids than amides, and hence that the amido-group which they contain is analogous to that in the amic acids. C. F. B.

Derivatives of Allophanic Acid. By W. TRAUBE (*Ber.*, **22**, 1572—1579).—*Benzyl allophanate* is formed by the action of gaseous cyanic acid on benzyl alcohol, benzyl carbamate being produced at the same time. The two can be separated by means of cold alcohol, which dissolves the carbamate. The residual allophanate, when crystallised from boiling water, yields glistening white needles. It melts at 183°, and at a higher temperature decomposes into cyanic acid and benzyl alcohol. It is soluble in ether and benzene, and in boiling alcohol or water. When heated with aqueous ammonia at 100°, it is converted into biuret. With alkalis it decomposes into ammonia, carbonic anhydride, and benzyl alcohol. When digested with benzyl alcohol at 110°, it yields benzyl carbamate, which crystallises in scales and melts at 86°. On the other hand, benzyl carbamate readily absorbs cyanic acid vapour, being converted into benzyl allophanate.

When benzyl carbamate is heated at 150° with phenyl isocyanate, *benzyl phenylallophanate*, $NHPh\cdot CO\cdot NH\cdot COOC_7H_7$, is formed. This is crystalline, easily soluble in alcohol, ether, and boiling water, melts at 158°, and decomposes at a slightly higher temperature. Other salts of isocyanic acid yield corresponding derivatives.

Lactic and cyanic acids do not react together, but when gaseous cyanic acid is passed into an ethereal solution of ethyl lactate as long as it is absorbed, and then the whole allowed to remain in a closed vessel, *ethyl allophanyllactate*, $NH_2\cdot CO\cdot NH\cdot CO\cdot O\cdot CHMe\cdot COOEt$, crystallises out in colourless needles. It is easily soluble in boiling water and alcohol, almost insoluble in ether and benzene, and melts at 170°. With alkalis it decomposes into carbonic anhydride, ammonia, alcohol, and lactic acid; treated with ammonia it yields biuret. When heated with concentrated hydrochloric acid on the water-bath, *allophanyllactic acid*, $C_5H_8O_5N_2$, is liberated. This acid crystallises in colourless, microscopic needles, sparingly soluble in cold water, easily so in boiling alcohol or water. It melts at 190° to a clear liquid, which almost immediately begins to evolve cyanic acid, lactic acid being left. The *alkali salts* form hard glass-like solids; the *silver salt* a white powder (which decomposes when boiled with water); and the *lead salt* a crystalline precipitate. The *ethyl salt* may be obtained by the action of amyl alcohol on the acid in the presence of gaseous hydrogen chloride, or by the action of cyanic acid on amyl lactate. It melts at 131°, is soluble in alcohol and ether, sparingly so in boiling water.

When ethyl glycollate is treated with gaseous cyanic acid, *ethyl allophanylglycollate*, $NH_2\cdot CO\cdot NH\cdot CO\cdot O\cdot CH_2\cdot COOEt$, is formed. This is sparingly soluble in benzene and ether, easily so in boiling water and alcohol. It crystallises in glistening scales or long needles, and melts at 144°. It is isomeric with Saytzeff's oxyethylglycolylallophanic acid. The *free acid* forms crystals, easily soluble in alcohol and water, and melting at 192°. The *alkali salts* are easily soluble; the *silver salt* forms a crystalline precipitate; the *copper salt* a sparingly soluble green powder.

The author was unable to obtain any allophanyl-derivatives from citric or isobutyric ethers, or from those of hydroxy-aromatic acids.

Ethyl tartrate yields with gaseous cyanic acid *ethyl allophanyltartrate*, $(C_2O_2N_2H_3)\cdot C_4H_3O_6Et_2$. It is crystalline, soluble in boiling water or alcohol, and melts at 188°. The *free acid* forms a syrup; the *silver salt* a heavy white precipitate.

When cyanic acid is passed into an ethereal solution of resorcinol, *resorcinol allophanate*, $C_8H_8O_4N_2$, is formed. It is sparingly soluble in ether, easily in boiling alcohol and water, and melts at 120°.

All these compounds decompose into their constituents at temperatures slightly above their melting points, or by the action of alkalis. L. T. T.

Chlorobromoparaxylenes and their Derivatives. By C. Willgerodt and R. Wolfien (*J. pr. Chem.* [2], **39**, 402—412).—*Chlorobromoparaxylene*, C_8H_8ClBr, is obtained by shaking a mixture of 10 grams of chloroparaxylene (b. p. 183—184°) and iron filings with bromine (11·5 grams). After cooling, the crystalline mass is dissolved in alcohol, filtered, and precipitated with water. It crystallises in pearly laminæ, melting at 66°, and becoming brown on exposure to light.

Chlorodibromoparaxylene is obtained when bromine (3·8 grams) is dropped into a mixture of chlorobromoparaxylene (5 grams) and iron filings. After two days, the mass is washed with cold alcohol, heated with alcohol, and filtered; on cooling, the chlorodibromoparaxylene remains in solution. It forms white needles, soluble in most organic solvents, and melts at 93°.

Chlorotribromoparaxylene [$Me_2 : Cl : Br_3 = 1 : 4 : 2 : 3 : 5 : 6$] is obtained when 10 grams of chloroparaxylene is mixed with iron filings and shaken with 34·2 grams of bromine; the product is crystallised from hot alcohol, or heated, when the tribromo-compound sublimes in white needles, which melt at 234° and are soluble in organic solvents.

Dichlorobromoparaxylene is obtained by mixing 5 grams of dichloroparaxylene (m. p. 66°) with iron and 4·6 grams of bromine. After three days the product is shaken with cold alcohol and dissolved in hot alcohol. On cooling, *dichlorodibromoparaxylene* crystallises out, and the dichlorobromoparaxylene remains in solution. It crystallises in white needles, which melts at 96° (uncorr.), and are soluble in most organic solvents.

Dichlorodibromoparaxylene, obtained as above described, forms white needles which melt at 226° and sublime.

Trichlorobromoparaxylene is formed when chlorine is passed through chlorobromoparaxylene containing iron filings; it crystallises in white needles which sublime and melt at 219°.

Nitrobromochloroparaxylene is prepared by acting on chlorobromoparaxylene (10 grams) with fuming nitric acid (50 grams), and pouring the liquid into water; it forms yellowish needles, soluble in organic solvents and melting at 99·5°.

Dinitrochlorobromoparaxylene, obtained by treating the last compound with fuming nitric acid, forms small, white crystals, insoluble in ether and alcohol, soluble in hot glacial acetic acid, chloroform, and benzene, and melting at 245° (uncorr.).

Chlorobromotoluic acid, $C_6H_2ClBrMe{\cdot}COOH$, is obtained when chlorobromoparaxylene (5 grams) is heated with chromic acid (11·4 grams) for six hours on the water-bath; the product, freed from acetic acid by a current of steam, is dissolved in soda and precipitated with sulphuric acid. It crystallises from ether in white laminæ melting at 185°. Its *barium* salt (with 1 mol. H_2O) was obtained.

Chlorobromoterephthalic acid is formed when chlorobromoparaxylene (1 gram) is heated with nitric acid of sp. gr. 1·1 (30 c.c.) in a sealed tube for four hours at 200°. It does not melt, but sublimes at 200—300°, and is soluble in organic solvents. Its *barium* salt (with 1 mol. H_2O) was obtained.

Chlorobromonitrotoluic acid is obtained by heating chlorobromotoluic acid with fuming nitric acid, and pouring the liquid into water; it crystallises in needles, which sublime above 200°, melt at 220° (uncorr.), distil with steam, and are soluble in organic solvents. Its *barium* salt (with 1 mol. H_2O) was obtained.

Nitrochlorobromoterephthalic acid, formed by heating chlorobromoterephthalic acid with fuming nitric acid, sublimes above 200°, and melts about 300°. Its *barium* salt crystallises with 1 mol. H_2O.

A. G. B.

Preparation of Durene and of Benzyldurene. By BEAUREPAIRE (*Bull. Soc. Chim.*, **50**, 676—679).—To obtain a satisfactory yield of durene from toluene and methyl chloride by Friedel and Craft's reaction, the author found it necessary to pass the methyl chloride through a narrow column at least 30 cm. high of the mixed toluene, and aluminium chloride at 95—96° under a pressure of 300—400 mm. of mercury. Proceeding thus 400 grams of toluene gave 180 grams of crude durene.

Benzyldurene, $C_6HMe_4{\cdot}CH_2Ph$, was prepared by heating for 11 hours in a flask provided with a reflux condenser, a mixture of durene (10 grams), benzyl chloride (7 grams), and carbon bisulphide (50 grams), with traces of aluminium chloride. On fractionation of the tarry liquid left after distilling off the bisulphide, it yielded a substance boiling at 300—350°, which after repeated crystallisation from glacial acetic acid, gave white, lustrous scales of monobenzyldurene. This compound is very soluble in glacial acetic acid, ether, and carbon bisulphide, but only slightly in alcohol; it melts at 145°, and distils at 325—327°.

T. G. N.

Desmotropy in Phenols. By J. HERZIG and S. ZEISEL (*Monatsh.*, **10**, 144—155).—In continuation of their former investigations (Abstr., 1888, 822, and this vol., p. 247) which show that from an alkaline solution of phloroglucinol and ethyl iodide, no triethoxybenzene is obtained, but only pentethylphloroglucinol, hexethyltriketohexomethylene, and bi-secondary ethyl-derivatives of phloroglucinol, the authors have examined the behaviour of other phenols in alkaline solution with ethyl iodide. They have, as expected, only obtained positive results with those phenols capable of giving rise to compounds containing the ketonic group $\cdot CO\cdot CH_2\cdot CO\cdot$, for only under such circumstances can an ethyl-group readily displace a hydrogen-atom, and even in this case there is a tendency for the ketonic compound to be reconverted into the phenolic form. These conditions obtain in phenols with at least two hydroxyl-groups, and these in the meta-position.

The authors show that by the action of ethyl iodide on resorcinol, diresorcinol, hydroxyhydroquinone, and potassium pyrogallate, there are formed, in addition to the characteristic ethoxybenzenes, oils which are insoluble in potash, and contain considerably less ethoxyl and more carbon and hydrogen than would be obtained from the diethoxy- or triethoxy-benzenes corresponding with the dihydroxy- or trihydroxy-benzenes with which the experiments were made. Similar experiments with dihydroxybenzoic acid [$COOH : (OH)_2 = 1 : 3 : 5$] show that the presence of a carboxyl-group seems to hinder the expected change.

Catechol diethyl ether, contrary to the statement of Koelle (*Annalen*, **159**, 245), is not a liquid at ordinary temperatures, but melts at 43—45°. Quinol diethyl ether seems to melt at 70—72°, which is in agreement with the temperature given by Rakowsky, and disproves that given by Nietzki. G. T. M.

Action of Chlorine on Phloroglucinol. By T. ZINCKE and O. KEGEL (*Ber.*, **22**, 1467—1477).—*Hexachlorotriketohexylene*, $CO<\begin{matrix}CCl_2\cdot CO\\ CCl_2\cdot CO\end{matrix}>CCl_2$, is formed when excess of chlorine is passed into a cooled chloroform solution of anhydrous phloroglucinol, moisture being carefully excluded. The filtered solution is evaporated on the water-bath, the residue fractionated under diminished pressure, and the portions passing over above 140—145° collected separately; the yield is 80—90 per cent. of the theoretical. It forms long, flat, spear-shaped crystals or broad plates, melts at 48°, boils at 268—269° (150—151°; 18—20 mm.), and is readily soluble in ether, benzene, chloroform, and carbon bisulphide. It liberates iodine from potassium iodide, combines with aniline yielding crystalline compounds, and is reduced to trichlorophloroglucinol when treated with stannous chloride in alcoholic solution. It decomposes slowly on exposure to moist air, and it is rapidly decomposed and dissolved by water, with evolution of carbonic anhydride and formation of equal quantities of dichloracetic acid and symmetrical tetrachloracetone. It is decomposed by cold alcohol, yielding small quantities of tetrachloracetone and ethyl dichloracetate, but the principal product is a colourless liquid, boiling at 239°, with slight decomposition (133—134°; 19—20° mm.), and insoluble in water. The last-named compound (b. p. 239°) yields dichloracetic acid when hydrolysed with alcoholic potash.

Trichlorophloroglucinol, prepared by reducing hexachlorotriketohexylene with stannous chloride in acetic acid solution, crystallises from alcohol or acetic acid in thick, colourless needles containing 3 mols. H_2O, and melts at 134°; the anhydrous substance melts at 108—109° (compare Hazura and Benedict, Abstr., 1886, 52, and Webster, Trans., 1885, 423). The *acetyl*-derivative, $C_6Cl_3(OAc)_3$, crystallises from dilute acetic acid in small plates, melting at 167—168°.

When pure phloroglucinol is treated with chlorine in cold, dilute, (1 : 100) aqueous solution, trichlorophloroglucinol separates at first in small crystals, but it gradually redissolves with evolution of carbonic anhydride; the solution contains dichloracetic acid and symmetrical tetrachloracetone, which is subsequently obtained in the form of the hydrate (+ $4H_2O$) (compare Hlasiwetz and Habermann, *Annalen*, **155**, 132). F. S. K.

Derivatives of Symmetrical Dihydroxyquinone. By R. Nietzki and F. Schmidt (*Ber.*, **22**, 1653—1662; compare Abstr., 1888, 1181).—Dianilidoquinone, $C_6H_2O_2(NHPh)_2$ [O : NHPh : O : NHPh = 1 : 2 : 4 : 5], is obtained by heating symmetrical dihydroxyquinone with aniline, and crystallises in lustrous, steel-blue scales; it is practically insoluble in all indifferent solvents, dissolves in concentrated sulphuric acid with a violet colour, and is identical with the dianilidoquinone prepared by Hofmann by the action of aniline on quinone.

Dihydroxyquinonedioxime (*loc. cit.*), on reduction with stannous chloride and hydrochloric acid, is converted into *diamidoquinol*, which can best be separated from the solution by the addition of dilute sulphuric acid; the *sulphate*, $C_6H_2(OH)_2(NH_2)_2,H_2SO_4$, which is precipitated, crystallises in sparingly soluble, colourless needles. When a salt of diamidoquinol is oxidised in aqueous solution by ferric chloride or in ammoniacal solution by atmospheric oxygen, a compound, $C_6H_6N_2O_2$, which may be either a diamidoquinone or a diimidoquinol, is formed; it crystallises in red needles with a violet iridescence, and dissolves in concentrated acids with a violet colour. On acetylation with sodium acetate and acetic anhydride, diamidoquinol hydrochloride or sulphate is converted into a *tetracetyl*-derivative, $C_6H_2(OAc)_2(NHAc)_2$, which crystallises in colourless needles, melts at 225°, and is soluble in warm alkali. The alkaline solution is not affected by exposure to the air, but if it is acidified and oxidised with ferric chloride, *acetylamidohydroxyquinone*, $NHAc{\cdot}C_6H_2O_2{\cdot}OH$, is obtained; this crystallises in golden-yellow scales, melts at 170°, and sublimes without decomposition at a higher temperature.

Nitrodiimidoquinol, $NO_2{\cdot}C_6H(OH)_2(NH)_2$, probably

$$[OH : NH : NO_2 : OH : NH = 1 : 2 : 3 : 4 : 5],$$

is formed by oxidising diamidoquinol sulphate, dissolved in acetic acid, with an equal quantity of nitric acid (sp. gr. = 1·4). It crystallises from alcohol in small, orange-red needles, or short, thick prisms, and on reduction with stannous chloride and hydrochloric acid, and subsequent addition of dilute sulphuric acid and alcohol, yields the sparingly soluble *triamidoquinol sulphate*, $[C_6H(NH_2)_3(OH)_2]_2,3H_2SO_4$, which crystallises in colourless needles, forms azines on treatment with orthodiketones, and is oxidised by ferric chloride, or in the case of an ammoniacal solution by atmospheric oxygen, with the formation of an amide crystallising in red needles.

The potassium-derivative of *nitrodihydroxyquinone* is obtained on warming nitrodiimidoquinol with dilute aqueous potash. It can also be prepared by oxidising the sulphate of symmetrical diamidoresorcinol suspended in acetic acid with an equal weight of nitric acid, and warming the resulting *nitrodiimidoresorcinol*, $C_6H_5N_3O_4$, with 10—15 times its weight of 10 per cent. aqueous potash. The *potassium*-derivative, $NO_2 \cdot C_6HO_2(OK)_2$, crystallises in stellate groups of small, orange-yellow needles, is readily soluble in water, from which it can be separated by the addition of alcohol or aqueous potash, and on precipitation with barium chloride yields a crystalline *barium* salt, from which nitrodihydroxyquinone can be obtained in readily soluble, golden-yellow needles, by decomposition with sulphuric acid.

Amidotetrahydroxybenzene hydrochloride, $NH_2 \cdot CH(OH)_4,HCl + H_2O$, is formed when nitrodihydroxyquinone is reduced with stannous chloride and hydrochloric acid, and crystallises in flat, silvery needles. On acetylation with sodium acetate and acetic anhydride, it yields a *pentacetyl*-derivative, $NHAc \cdot C_6H(OAc)_4$, which crystallises from alcohol in colourless needles, and melts at 242° with decomposition. It has not been found possible to prepare pentahydroxybenzene from amidotetrahydroxybenzene.

The authors discuss the view put forward by Nef (this vol., p. 497), that nitranilic acid is not a derivative of dihydroxyquinone but of dihydrodiquinoyl, and point out that the constitution of chloranilic and bromanilic acids and of dihydroxyquinone must be similar to that of nitranilic acid. Against Nef's view, they urge that these compounds do not react with orthodiamines to form azines, that whilst true diquinoyl-derivatives such as rhodizonic and leuconic acids yield carbonic anhydride on treatment with alkalis, the three anilic acids are extremely stable in the presence of alkalis; and that though dihydroxyquinone is affected by boiling with alkalis it differs from diquinoyl-derivatives in being completely decomposed thereby.

W. P. W.

Tolunitranilic Acid: some Nitro-derivatives of Toluquinol. By F. Kehrmann and R. Brasch (*J. pr. Chem.* [2], **39**, 377—391; compare Abstr., 1888, 940).—To obtain *tolunitranilic acid* (*nitrodihydroxytoluquinone*), a mixture (200 grams) of tetra-, di-, and trichlorotoluquinones, prepared by chlorinating crude coal-tar cresol, is warmed with sufficient 25 per cent. alcohol to make a thin cream, and powdered potassium nitrite added by degrees, until no more yellow particles are left, alcohol being added from time to time to make up for that lost as ethyl nitrite. The crystalline mass is drained, washed with alcohol, and dissolved in a little hot water; when cold, potassium nitranilate crystallises and is filtered off; a little strong potash is now added to precipitate the rest of the nitranilate, and then more potash until the *potassium* tolunitranilate, $C_6O_2(OK)_2Me \cdot NO_2 + 3Aq$, is all thrown down. This salt crystallises in long, yellowish-red prisms, easily soluble in hot water. The free acid forms long, golden-yellow needles (containing water of crystallisation), which melt with decomposition at 180°; its aqueous solution decomposes on boiling with formation of carbonic anhydride, hydrogen cyanide, and oxalic acid. The *sodium* and *ammonium* salts are described, and also the precipitates which these salts give with solutions of other metallic salts; the *barium* and *acid potassium* salt were obtained.

Paranitrotetrahydroxytoluene, $NO_2 \cdot C_6Me(OH)_4$, is obtained by the action of stannous chloride on potassium tolunitranilate dissolved in hydrochloric acid; it forms lustrous, pitch-black, prismatic crystals, which give a brownish-violet streak, and are easily soluble in hot water, alcohol, and ether. Its solution is decomposed by prolonged boiling.

Tolunitranilic acid was not obtained by nitrating diacetyl-toluquinol.

Acetyl-dinitrotoluquinol, $C_9H_8N_2O_7$, is obtained by acting on diacetyltoluquinol with nitric acid (sp. gr. 1·4) at 0°. The yield is 60 to 70 per cent. of the diacetyltoluquinol. It crystallises from chloroform in brilliant, transparent, citron-yellow polyhedra, melts at 144—146°, and is freely soluble in chloroform, hot alcohol, and benzene. The *potassium* compound forms brilliant, garnet-red, slender prisms, which detonate when heated and are easily soluble in hot water.

Diacetyl-dinitrotoluquinol is formed when acetyl-dinitrotoluquinol is heated with acetic anhydride and sodium acetate; it crystallises from hot glacial acetic acid in colourless silky needles, melting at 154—157°.

Dinitrotoluquinol, $C_6HMe(NO_2)_2(OH)_2$, is obtained from either of the above acetyl-derivatives by saponifying it with cold dilute alkali; it crystallises from 50 per cent. alcohol in large, yellowish-red, efflorescent prisms or tables (with 1 mol. H_2O); the anhydrous substance melts at 149—153°; it is insoluble in cold water. It forms two series of derivatives with bases, the primary, which are crystalline, dark brownish-red, easily soluble in water but insoluble in alcohol; and the secondary, which do not crystallise, and give dark violet solutions. The *primary potassium*-derivative is described.

Nitramidotoluquinol hydrochloride, formed by reducing the dinitro-derivative with the calculated quantity of stannous chloride, crystallises from hot dilute hydrochloric acid in beautiful, long, yellowish-brown needles, which become laminæ if left in the liquid. By further reduction with stannous chloride, it yields *diamidotoluquinol hydrochloride;* this is obtained with some difficulty as large colourless prisms (with H_2O), which are easily soluble in water and hydrochloric acid.

The authors discuss the structural formulæ of the foregoing substances. A. G. B.

New Franceïn from 1 : 3 : 4 : 5-Tetrachlorobenzene. By Georgesco and Mincou

(*Bull. Soc. Chim.*, 50, 623—625).—By the action of sulphuric acid on 1 : 3 : 4 : 5-tetrachlorobenzene, the authors have obtained a franceïn isomeric with that prepared by Istrati, in like manner from 1 : 2 : 4 : 5-tetrachlorobenzene (Abstr., 1888, 259). It forms greenish-black fragments, having a metallic lustre; when powdered it is quite black. It is soluble in alkalis, but only dissolves slightly in alcohol and glycerol, forming reddish solutions which do not show dichroism. It appears to have the formula $C_{16}H_4O_6Cl_3$, the whole of the hydrogen being replaceable by silver. T. G. N.

Action of Zinc Chloride on Acetanilide. By A. PICTET and R. BUNZL (*Ber.*, **22**, 1847—1850).—When equal weights of zinc chloride and ethylacetanilide are heated at 250—260° until no further reaction takes place, a mixture of quinaldine, acetylparamidoethylbenzene, paramidoethylbenzene, acetic acid, and a secondary base, probably either ethylaniline or tetrahydroquinaldine, is obtained. Ethylaniline is known to undergo conversion into paramidoethylbenzene when heated with zinc chloride (Hofmann, Abstr., 1874, 807; Benz, Abstr., 1882, 1284), and the presence of acetylparamidoethylbenzene, together with the products of its hydrolysis, paramidoethylbenzene and acetic acid, in the melt can be accounted for by a like isomeric change. The formation of quinaldine instead of lepidine can be explained if ethylacetanilide yields ortho- as well as para-acetamidoethylbenzene, the former then undergoing condensation; in confirmation of this view the authors find that acetylorthamidoethylbenzene is converted into quinaldine when heated with zinc chloride at 170°. W. P. W.

Trinitrophenylmethylnitramine. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, 8, 215—216).—This substance was synthesised by mixing alcoholic solutions of methyl nitramine and picryl chloride, and adding water after the reaction had taken place. The substance precipitated was washed with cold alcohol; it consisted of small, yellow crystals melting at 127°, and was shown by analysis to have the formula $C_7H_5N_5O_8$. This substance is identical with the product obtained by the action of nitric acid on methylaniline or dimethylaniline, and is therefore trinitrophenylmethylnitramine, having the formula $C_6H_2(NO_2)_3{\cdot}NMe{\cdot}NO_2$ [= 2 : 4 : 6 : 1]. C. F. B.

Action of Chromic Anhydride on Alkylanilines. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, 8, 248—253).—The action of chromic anhydride on dialkyldinitroanilines of the general formula

$$C_6H_3(NO_2)_2{\cdot}NR_2,\ 4:2:1$$

is described. The first reaction gives a monalkylaniline,

$$C_6H_3(NO_2)_2{\cdot}NHR,$$

with separation of the aldehyde, which is further oxidised to the acid; one of the alkyl-groups is thus displaced by hydrogen. The monalkyl-derivative when treated with potash gives the alkylamine and a dinitrophenol; on further oxidation with chromic anhydride, it gives dinitraniline. Dinitrodimethylaniline (4 : 2 : 1) was dissolved in acetic acid, and to the boiling solution a solution of chromic anhydride was added little by little; the whole was then thrown into water, when dinitromethylaniline melting at 178° separated. This when boiled with potash gave methylamine. Dinitrodiethylaniline (4 : 2 : 1) treated in the same way gave dinitroethylaniline melting at 113°; this with potash gives ethylamine; on further oxidation with chromic anhydride, it gives dinitraniline melting at 175°.

Dinitrodipropylaniline, $C_6H_3(NO_2)_2{\cdot}NPr_2^{\alpha}$, 4 : 2 : 1, was prepared by the action of dipropylamine on dinitrobromobenzene; it forms large, yellow crystals melting at 40°. When oxidised with chromic anhydride, it gives first dinitropropylaniline melting at 97°, and then dinitroaniline melting at 175°.

With para- and meta-dinitroalkylanilines, definite results were not obtained. A dinitrodimethylaniline (obtained by the action of nitric acid on dimethylaniline dissolved in excess of sulphuric acid), when oxidised with chromic anhydride, gave crystals of dinitromethylaniline, $C_6H_3(NO_2)_2{\cdot}NHMe = 3 : X : 1$.

Further results are to be communicated in a future paper.

C. F. B.

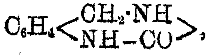
Derivatives of Orthamidobenzyl Alcohol. By H. G. SÖDERBAUM and O. WIDMAN (*Ber.*, **22**, 1665—1672).—Acetyl-derivatives are formed when orthamidobenzyl alcohol is treated with acetic anhydride, but there is no tendency for condensation to take place with the production of cumazone-derivatives (compare Widman, Abstr., 1884, 302).

Orthacetamidobenzyl alcohol, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, crystallises from benzene in long needles, melts at 114°, and on treatment with dilute acids in the cold, or more rapidly on warming, is reconverted into orthamidobenzyl alcohol. The *platinochloride*, $(C_9H_{11}NO_2)_2,H_2PtCl_6$, crystallises in long, flat, serrated forms. *Orthacetamidobenzyl acetate*, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}OAc$, is formed by heating the amido-alcohol with excess of acetic anhydride for a short time. It crystallises in stellate groups of flat needles, melts at 91°, and is very soluble in benzene. When dissolved in hydrochloric acid and allowed to remain at the ordinary temperature for about four hours, it is converted into *orthamidobenzyl acetate*, a yellow oil which yields a *hydrochloride*, $C_9H_{11}NO_2,HCl$, crystallising in slender, white needles, and a *platinochloride*, $(C_9H_{11}NO_2)_2,H_2PtCl_6$, crystallising in four-sided tables or serrated, flat needles. *Orthodiacetamidobenzyl acetate*,

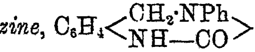
$$NAc_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OAc,$$

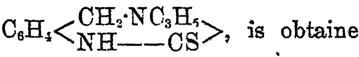
is prepared by heating the amido-alcohol for two hours with an excess of acetic anhydride, and is an oil which could not be obtained in the solid state.

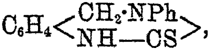
ω-Hydroxytolylcarbamide, $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CONH_2$, obtained in the ordinary way from orthamidobenzyl alcohol, potassium cyanate, and hydrochloric acid, crystallises in four-sided tables, melts at about 180° with decomposition, and is soluble in hot water, sparingly soluble in benzene, alcohol, acetone, &c. Heated at 180° until ammonia ceases to be evolved, it is converted into *dihydroxytolylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH)_2$, which crystallises from benzene in very slender needles and melts at 108°. *Phendihydroketometadiazine*,



$C_6H_4{<}\begin{matrix}CH_2{\cdot}NH\\NH{-}CO\end{matrix}{>}$, is formed by heating hydroxytolylcarbamide with concentrated hydrochloric acid for about 45 minutes at 100°. It crystallises from benzene in thin, lustrous scales, melts at 160°, is practically insoluble in cold though somewhat readily soluble in hot concentrated aqueous potash, and dissolves readily in dilute acids forming readily soluble salts. The *hydrochloride* crystallises in flat needles; the *platinochloride*, $(C_8H_8N_2O)_2,H_2PtCl_6 + 2H_2O$, crystallises in stellar aggregates and melts at 204—205° with decomposition; the *aurochloride*, $C_8H_8N_2O,HAuCl_4$, forms lustrous, golden-yellow scales and melts at 179° with decomposition.

ω-Hydroxytolylphenylcarbamide, $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh$, crystallises in slender, pointed needles, melts at 191°, and is very sparingly soluble in the ordinary solvents. When warmed with hydrochloric acid on a water-bath, it is converted into *benzophenyldihydroketometadiazine*,  $C_6H_4{<}\begin{matrix}CH_2{\cdot}NPh\\NH{-}CO\end{matrix}{>}$, which crystallises from benzene in rosettes of flat needles and melts at 143°.

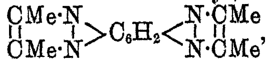
Phenallyldihydrothiometadiazine,  $C_6H_4{<}\begin{matrix}CH_2{\cdot}NC_3H_5\\NH{-}{-}CS\end{matrix}{>}$, is obtained by dissolving equimolecular proportions of orthamidobenzyl alcohol and allylthiocarbimide in benzene and warming the resulting oily ω-hydroxytolylallythiocarbamide with dilute hydrochloric acid at 100°. It crystallises in very slender, white, felted needles, melts at 90—91°, and is very soluble in alcohol, benzene, and acetone.

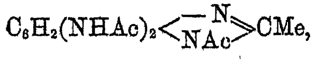
ω-Hydroxytolylphenylthiocarbamide, $OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHPh$, crystallises in colourless, four-sided prisms and melts at 136°. When warmed with concentrated hydrochloric acid for a short time, it is converted into *benzophenyldihydrothiometadiazine*,  $C_6H_4{<}\begin{matrix}CH_2{\cdot}NPh\\NH{-}CS\end{matrix}{>}$, which crystallises in stellate groups of flat needles, melts at 197°, and is insoluble in hot concentrated aqueous potash. The *platinochloride*, $(C_{14}H_{12}N_2S)_2,H_2PtCl_6$, is an orange, crystalline powder and melts at 219° with decomposition; the *aurochloride*, $C_{14}H_{12}N_2S,HAuCl_4$, forms short, yellow needles and melts at 197° with decomposition.

W. P. W.

Oxidation of Paraphenylenediamine and of Paramidophenol. By E. v. BANDROWSKI (*Monatsh.*, **10**, 123—128; compare this vol., p. 449).—If an ammoniacal solution of paraphenylenediamine, or preferably of its hydrochloride, is left exposed to the air, dark-green acicular crystals, having a reddish colour by transmitted light, are formed on the surface. The oxidation takes place more rapidly on passing oxygen through the solution or on adding to it peroxide of hydrogen or potassium ferricyanide, the reaction being quantitative in the last case. The new compound has the formula $C_6H_6N_2$, is only slightly soluble in water, more soluble in alcohol and in benzene, melts at 230—231°, has feeble basic properties, and forms with acetic anhydride an acetyl-derivative, $C_6H_5N_2Ac$, crystallising from nitrobenzene in beautiful pink crystals, which melt with decomposition at 294°, and are only very sparingly soluble in ordinary solvents. The formation of this monacetyl-derivative seems to show that the substance is not an hydrazophenylene, and this view is confirmed by its high melting point, its insolubility, and the fact that paraphenylenediamine is not regenerated on treating it with reducing agents.

When oxidised under similar circumstances to those above mentioned, paramidophenol yields a compound of the formula C_6H_5NO. It forms dark green crystals having a reddish shimmer, melts with decomposition at 228°, is insoluble in chloroform and benzene, only slightly soluble in water and dissolves readily in alcohol. It gives a blue coloration with acids, and this is so intense, when sulphuric acid is employed, that the minutest quantity of the substance may be readily recognised. It dissolves readily in alkalis, forming reddish-violet solutions, from which it is thrown out on neutralisation with an acid. The general behaviour of the compound, especially in regard to its neither forming an acetyl-derivative nor giving paramidophenol when treated with reducing agents, seems to show that it is not imidoquinone. G. T. M.

Consecutive Tetramidobenzene. By R. NIETZKI and L. SCHMIDT (*Ber.*, **22**, 1648—1653).—1 : 2 : 3 : 4-Diquinoyltetroxime (Goldschmidt and Strauss, Abstr., 1887, 808) can be reduced by careful treatment with a solution of stannous chloride in hydrochloric acid, and the resulting tetramidobenzene is best separated in the form of its sparingly soluble sulphate by the addition of dilute sulphuric acid and alcohol to the solution. 1 : 2 : 3 : 4-*Tetramidobenzene sulphate*, $C_6H_2(NH_2)_4,H_2SO_4$, crystallises in colourless scales and is very sparingly soluble in water, but readily soluble in concentrated hydrochloric acid. The *base* is very rapidly oxidised on exposure to air, and is distinguished from the symmetrical tetramidobenzene (Abstr., 1887, 476) by being less basic; with the exception of the sulphate, the salts are very readily soluble and could not be obtained in a state fit for analysis. On treatment with diacetyl, the sulphate is converted into a *diquinoxaline*,  $\begin{matrix}CMe\cdot N\\ \| \quad\ |\\ CMe\cdot N\end{matrix}>C_6H_2<\begin{matrix}N\cdot CMe\\ | \quad\ \|\\ N\cdot CMe\end{matrix}$, which crystallises in slender, golden-yellow needles and melts at 218°. When acetylated by heating with anhydrous sodium acetate and acetic anhydride at 100°, the sulphate yields a compound, $C_{14}H_{16}N_4O_4$, crystallising in long, colourless, silky needles melting at 260°. Although the analytical numbers seem to indicate that the substance is a tetracetyl-derivative, it is more probable that it is a *triacetylated ethenyl-base*,



$$C_6H_2(NHAc)_2<{{-N} \atop {NAc}}>CMe,$$

crystallised with 1 mol. H_2O, and its ready solubility in dilute acids seems to confirm this view. When it is dissolved in dilute hydrochloric acid and precipitated by ammonia, a compound, $C_{12}H_{14}N_4O_2$, is formed to which the formula $C_6H_2(NHAc)_2<{{-N} \atop {NH}}>CMe$ is assigned. This crystallises in colourless needles, melts at 176°, yields a *picrate*, $C_{12}H_{14}N_4O_2,C_6H_3N_3O_7$, crystallising in yellow needles, and when heated with acetic anhydride is reconverted into the triacetyl-base.

Diethenyltetramidobenzene, $C_6H_2\left(<{{-N} \atop {NH}}>CMe\right)_2$, is obtained as sulphate by dissolving either the di- or tri-acetylethenyl base in dilute sulphuric acid and evaporating the solution to dryness. The base crystallises in colourless needles, melts at 145°, forms a *platinochloride*, $C_{10}H_{10}N_4,H_2PtCl_6$, crystallising in yellow needles, and a *picrate*, $C_{10}H_{10}N_4,2C_6H_3N_3O_7$, crystallising also in yellow needles. It is not, however, identical with the diethenyl-derivative of the 1 : 2 : 3 : 4-tetramidobenzene obtained by reducing diacetyldinitroparaphenylenediamine (Abstr., 1887, 476), and there is nothing to show which two of the three possible formulæ for diethenyl-1 : 2 : 3 : 4-tetramidobenzene should be respectively assigned to these isomerides.

W. P. W.

Decomposition of Diazo-compounds. By I. REMSEN and R. O. GRAHAM (*Amer. Chem. J.*, **11**, 319—331; compare Abstr., 1888, 268).—*Orthonitrodiazobenzene nitrate*, prepared by the action of nitrous anhydride on a nitric acid solution of orthonitraniline, forms small tabular crystals, which are at first white, but quickly become yellow. It is easily soluble in water and explodes when heated.

Orthonitrodiazobenzene sulphate crystallises in small colourless plates; it is very stable and explodes feebly when heated; when it is warmed with absolute alcohol, it yields aldehyde, nitrobenzene (54 per cent. of the theoretical yield) and a small quantity of solid substance which could not be purified.

Metanitrodiazobenzene sulphate, made by diazotising metanitroaniline sulphate, forms white, granular crystals; it deflagrates when heated by a free flame, leaving a black residue. When heated with alcohol, it yields aldehyde and nitrobenzene. Meta- and para-nitrodiazobenzene nitrates also yield aldehyde and nitrobenzene when heated with alcohol.

Griess (Abstr., 1888, 588) has investigated the action of alcohol on the diazobenzoic acids, but the authors' results differ from his in some respects. Orthodiazobenzoic acid nitrate heated with alcohol yielded ethyl benzoate (53 per cent. of theory); when heated in toluene, it gave asymmetrical nitrosalicylic acid [$COOH : OH : NO_2 = 1 : 2 : 4$]. Metadiazobenzoic acid sulphate also yielded ethyl benzoate (63 per cent. of theory) when heated with alcohol (compare Fittica, Abstr., 1878, 980); paradiazobenzoic acid nitrate, on the other hand, yielded only a little ethyl benzoate, the main product being paraethoxybenzoic acid; with methyl alcohol, it gave paramethoxybenzoic (anisic) acid; and with propyl alcohol, *parapropoxybenzoic acid*, which crystallises in lustrous plates nearly insoluble in water, easily soluble in alcohol, melting at 141·5—142·5°, and subliming; its *barium*, *silver*, *lead*, and *calcium* salts are described.

Paradiazobenzoic acid nitrate is decomposed by water between 80° and 90° with formation of the nitroxybenzoic acid described by Gruber (Abstr., 1879, 644), and paroxybenzoic acid. When heated with toluene, paradiazobenzoic acid nitrate yields the same nitro-acid as it does when heated with water.

From their results, the authors conclude that the presence of a nitro-group influences the diazo-group so that hydrogen can be substituted for it, whether it be in the ortho-, meta-, or para-position; but a carboxyl-group only influences an ortho- or a meta-diazo-group in this way.

A. G. B.

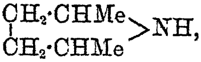
Reduction of Hydrazones. By J. TAFEL (*Ber.*, **22**, 1854—1860; compare Abstr., 1887, 467—470).—In preparing large quantities of amines by the reduction of the hydrazones the latter are dissolved or suspended in alcohol (10—20 parts), the solution mixed with glacial acetic acid (25 c.c.) and $2\frac{1}{2}$ per cent. sodium amalgam (250 grams) added in small quantities at a time with constant shaking, care being taken that no appreciable rise of temperature occurs. As soon as the whole of the sodium amalgam has been added, the solution is again mixed with glacial acetic acid (25 c.c.), and a further quantity (250 grams) of sodium amalgam added as before; this process is repeated until about twice the calculated quantity of sodium amalgam has been employed. The whole operation can be most conveniently carried out in the apparatus devised by the author. The solution is then saturated with soda and the bases distilled in an oil-bath, using steam if necessary. When aniline is present, the distillate is exactly neutralised with hydrochloric or sulphuric acid, and the solution, after concentrating, shaken with ether; the ethereal extract contains the whole of the aniline and generally resinous products as well, so that the aqueous solution contains the amine salt in an almost pure condition.

Pentylamine boils at 91·5° (755 mm.; thermometer entirely in vapour). The *hydrochloride*, $C_5H_{13}N,HCl$, crystallises from alcohol and ether in long, colourless needles, melts at 168°, and is readily soluble in water and in alcohol. The *oxalate*, $(C_5H_{13}N)_2,C_2H_2O_4$, crystallises from hot, dilute alcohol in thin plates melting at 230° with decomposition. The *acid oxalate*, $C_5H_{13}N,C_2H_2O_4$, melts at 131°, and is much more readily soluble in alcohol.

Phenylethylamine boils at 187·5° (763 mm.; thermometer entirely in vapour) and is soluble in about 24 parts of water at 20°. The hydrochloride melts at 158°. The oxalate, $(C_8H_{11}N_2)_2,C_2H_2O_4$, crystallises from hot water in compact prisms, melts at 238°, and is almost insoluble in alcohol. The *acid oxalate* separates in small, shining plates when the neutral salt is treated with an alcoholic solution of oxalic acid; it is readily soluble in cold water and is reconverted into the neutral salt when boiled with alcohol.

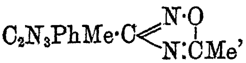
Phenylpropylamine is a colourless oil with a peculiar aromatic and only slightly ammoniacal smell; it boils at 221·5° (755 mm.; thermometer entirely in vapour). The *hydrochloride*, $C_9H_{13}N,HCl$, crystallises in small, shining plates, melts at 218°, and sublimes at 100°. The *sulphate*, $(C_9H_{13}N)_2,H_2SO_4$, crystallises from hot alcohol in thin prisms or plates, is readily soluble in water, and begins to decompose at 250°. The *oxalate*, $(C_9H_{13}N)_2,C_2H_2O_4$, crystallises in long needles and begins to melt at 156°, but when heated quickly it does not begin to decompose until about 170°; it is readily soluble in hot water, but is then partially converted into the acid salt. The *acid* oxalate, $C_9H_{13}N,C_2H_2O_4$, crystallises from warm water or hot alcohol in prisms melting at 156°. The *platinochloride*, $(C_9H_{13}N)_2,H_2PtCl_6$, crystallises from hot water in yellowish plates, decomposes at about 230°, and is almost insoluble in alcohol.

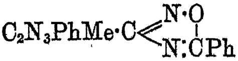
Diamidohexane, $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$, is obtained, together with aniline and dimethylpyrrolidine, by reducing acetonylacetonedihydrazone as described above at 30—32°. The mixture is freed from aniline, the hot, concentrated alkaline solution of the bases neutralised with an alcoholic solution of oxalic acid, the precipitated diamidohexane oxalate decomposed with alkalis and the base distilled over barium oxide. It is a colourless, ammoniacal smelling oil, boils at 175°, fumes in the air, and is miscible with water, alcohol, and ether in all proportions; the aqueous solution has a strong alkaline reaction, and on adding potash the base separates as an oil. The *oxalate*, $C_6H_{16}N_2,C_2H_2O_4$, crystallises from hot, dilute alcohol in small, slender needles, and is readily soluble in water but almost insoluble in alcohol.

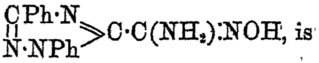
Dimethylpyrrolidine,  $\begin{matrix}\mathrm{CH_2{\cdot}CHMe} \\ | \\ \mathrm{CH_2{\cdot}CHMe}\end{matrix}\!>\!\mathrm{NH}$, remains as oxalate in the mother-liquors from the diamidohexane salt, and can be isolated by distilling with potash and fractionating over barium oxide and sodium. It is a colourless oil with a strong piperidine-like odour, boils at 106—108° (746 mm.; thermometer entirely in vapour), and is miscible with water, alcohol, and ether in all proportions. The aqueous solutions have a strongly alkaline reaction. It forms an oily *nitrosamine*; the latter gives Liebermann's reaction, and is readily reduced by zinc and acetic acid, yielding a compound—probably the hydrazine—which rapidly reduces Fehling's solution. The *oxalate*, $(C_6H_{13}N)_2,C_2H_2O_4$, crystallises from alcoholic ether in small, slender needles, and is readily soluble in water and alcohol. The *platinochloride*, $(C_6H_{13}N)_2,H_2PtCl_6$, crystallises from hot alcohol in golden prisms, and is readily soluble in water. F. S. K.

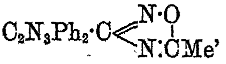
Conversion of Trinitrohydrazobenzene into Nitrosodinitroazobenzene. By M. FREUND (*Ber.*, 22, 1663—1665).—Trinitrohydrazobenzene (Fischer, Abstr., 1878, 309) does not yield a carbizin-derivative on treatment with a solution of carbonyl chloride in benzene (compare Freund and Goldsmith, Abstr., 1888, 686, 1187), but loses the elements of a molecule of water and is converted into *nitrosodinitroazobenzene*, $NPh{:}N{\cdot}C_6H_2(NO_2)_2{\cdot}NO$, which melts at 248°. A like change is effected by boiling with acetic acid, and hence it is the temperature employed, and not the presence of carbonyl chloride, which determines the formation of this compound. The presence in the molecule of the nitroso-group could not be detected by Liebermann's reaction, but is confirmed by the fact that the reddish-brown solution obtained by dissolving the compound in aniline yields on precipitation with alcohol slender, bronze-coloured scales melting at 222°. Nitrosodinitroazobenzene is identical with Willgerodt and Ferko's so-called dinitrosonitroazobenzene (Abstr., 1888, 829), to which the formula $C_{12}H_7N_5O_4$ has been erroneously assigned. W. P. W.

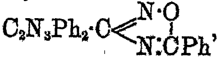
Amidoximes and Azoximes of the Triazole and Tetrazole Series. By J. A. BLADIN (*Ber.*, 22, 1748—1756; compare Abstr., 1887, 138).—Phenylmethyltriazenylamidoxime gives in alcoholic solution a deep-red coloration with ferric chloride. The *hydrochloride*, $C_{10}H_{11}N_5O,HCl$, is a crystalline compound readily soluble in water. The *platinochloride*, $(C_{10}H_{11}N_5O)_2,H_2PtCl_6$, forms yellow crystals, melts at 200—201° with decomposition, and is moderately easily soluble in hydrochloric acid. The *acetyl*-derivative, $C_{10}H_{10}N_5{\cdot}OAc$, prepared by warming the amidoxime with excess of acetic anhydride, crystallises from alcohol or benzene in small, flat needles, melts at 148°, and is very sparingly soluble in water and ether, but soluble in acids. It is reconverted into the amidoxime when boiled with potash. The *benzoyl*-derivative, $C_{10}H_{10}N_5\cdot OBz$, prepared by warming the amidoxime with excess of benzoic chloride, crystallises from alcohol in small, rectangular plates, melts at 183—183·5° with decomposition, and is insoluble in water and potash; it forms a sparingly soluble *hydrochloride.*

Phenylmethyltriazenylethenylazoxime,  $C_2N_3PhMe\cdot C<\begin{array}{l}N\cdot O\\ \mid \\ N{:}CMe\end{array}$, is obtained when the amidoxime is boiled with excess of acetic anhydride for 10 minutes; it crystallises from ether in small, colourless, flat needles, melts at 105·5°, and is very readily soluble in benzene and alcohol, and moderately so in ether, but only sparingly in water. It has basic properties and dissolves freely in mineral acids, but is insoluble in alkalis.

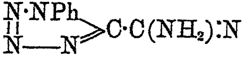
Phenylmethyltriazenylbenzenylazoxime,  $C_2N_3PhMe\cdot C<\begin{array}{l}N\cdot O\\ \mid \\ N{:}CPh\end{array}$, prepared by heating the benzoyl-derivative (see above) above its melting point, crystallises from alcohol in small, colourless needles, melts at 166—167°, and is insoluble in water; it is a very feeble base and dissolves only very slowly in hydrochloric acid.

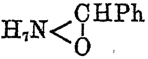
Diphenyltriazenylamidoxime,  $\begin{array}{l}CPh\cdot N\\ \| \\ N\cdot NPh\end{array}\!\!>C\cdot C(NH_2){:}NOH$, is prepared by treating an alcoholic solution of diphenylcyanotriazole (this vol., p. 702) with an aqueous solution of the calculated quantity of hydroxylamine. It crystallises from alcohol in colourless prisms containing ½ mol. H_2O, and from water in long needles, loses its water at 100°, melts at 213·5—214° with decomposition, and is readily soluble in hydrochloric acid, but only moderately so in potash. Alcoholic solutions give a deep-red coloration with ferric chloride. The *hydrochloride,* $C_{15}H_{13}N_5O,HCl$, is a colourless, crystalline compound. The *platinochloride* is readily soluble and is decomposed by hydrochloric acid. The *acetyl*-derivative, $C_{15}H_{12}N_5\cdot OAc$, prepared by dissolving the anhydrous amidoxime in warm acetic anhydride, crystallises from alcohol in small, colourless needles, melts at 176—177° with decomposition, is almost insoluble in water, and has basic properties. The *benzoyl*-derivative, $C_{15}H_{12}N_5\cdot OBz$, prepared by carefully warming the anhydrous amidoxime with excess of benzoic chloride, crystallises from alcohol in small, colourless plates, melts at 179—179·5° with decomposition, and is insoluble in water.

Diphenyltriazenylethenylazoxime,  $C_2N_3Ph_2\cdot C<\begin{array}{l}N\cdot O\\ \mid \\ N{:}CMe\end{array}$, is formed when the preceding compound is boiled with acetic anhydride, or when the acetyl-derivative thereof is heated above its melting point. It crystallises from alcohol in small, colourless prisms, melts at 152—153°, and is sparingly soluble in ether and insoluble in water and potash, but it dissolves slowly in hydrochloric acid.

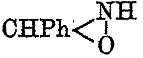
Diphenyltriazenylbenzenylazoxime,  $C_2N_3Ph_2\cdot C<\begin{array}{l}N\cdot O\\ \mid \\ N{:}CPh\end{array}$, is obtained

when the amidoxime is boiled for five minutes with excess of benzoic chloride, or when the benzoyl-derivative described above is heated above its melting point. It crystallises from alcohol in small, colourless needles, melts at 205·5—206°, and is insoluble in water.

Phenyltetrazenylamidoxime,  $\overset{N\cdot NPh}{\underset{N——N}{\|}}>C\cdot C(NH_2){:}NOH$, can be prepared by treating an alcoholic solution of phenylcyanotriazole with the calculated quantity of an aqueous solution of hydroxylamine and evaporating the alcohol on the water-bath. It separates from hot alcohol in colourless crystals, melts at 176—177·5° with decomposition, and is insoluble in water. It dissolves in alkalis and acids, but alcoholic solutions do not give a red coloration with ferric chloride. The *acetyl*-derivative, $C_8H_7N_6\cdot OAc$, obtained by heating the amidoxime with excess of acetic anhydride, crystallises from alcohol in small, slender needles, melts at 202—203° with decomposition, and is only very sparingly soluble in alcohol and insoluble in water; it has neither acid nor basic properties, and cannot be converted into the azoxime. The *benzoyl*-derivative, $C_8H_7N_6\cdot OBz$, prepared in like manner, crystallises from alcohol in microscopic needles, melts at 205—206° with decomposition, and is very sparingly soluble or insoluble in ordinary solvents. It resembles the acetyl-derivative in properties and cannot be converted into the azoxime. F. S. K.

Alkyl-derivatives of Hydroxylamine. By R. BEHREND (*Ber.*, **22**, 1433—1434).—Benzylisobenzaldoxime is formed when an ethereal solution of dibenzylhydroxylamine is shaken with an excess of an aqueous solution of potassium ferricyanide. This reaction is further evidence in support of the formula  $C_7H_7N<\overset{CHPh}{\underset{O}{|}}$ for Beckmann's benzylisobenzaldoxime. (Compare Behrend and Leuchs, this vol., p. 703.) F. S. K.

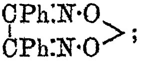
Isomerism of the Benzaldoximes. By E. BECKMANN (*Ber.*, **22**, 1531—1536; compare this vol., p. 608).—α-Benzylhydroxylamine hydrochloride is decomposed into ammonia and benzyl iodide when boiled for 15 hours with hydriodic acid; β-benzylhydroxylamine hydrochloride, on the other hand, is entirely converted into benzylamine. The two compounds have, therefore, the constitution $NH_2\cdot O\cdot CH_2Ph$ and $CH_2Ph\cdot NH\cdot OH$ respectively.

Benzyl α-benzaldoxime is decomposed by hydriodic acid, yielding ammonia and benzyl iodide, but the corresponding β-derivative gives benzylamine alone; the two compounds have, therefore, the constitution $CHPh{:}NOH$ and  $CHPh<\overset{NH}{\underset{O}{|}}$ respectively, in accordance with V. Meyer's view.

When α-benzaldoxime is dissolved in alcoholic potash and treated with benzyl chloride or ethyl iodide, the α-alkyl compound is not obtained in a pure state; if the product is dissolved in ether, and hydrogen chloride passed into the solution, oily or solid products are precipitated, and after evaporating the clear solution, the α-compound can be dissolved out by treating the residue with a little ether. Ethyl α-benzaldoxime thus prepared is obtained in the form of a colourless oil, which, when treated with hydriodic acid, yields ammonia, but no other basic substance. The hydrochloride undissolved by the ether behaves like the β-derivative, and yields ethylamine (or benzylamine) with hydriodic acid. In preparing alkyl β-benzaldoximes in a similar manner, compounds other than the β-derivative, and which behave like the α-derivatives, are formed in large quantities.

In preparing alkyl β-benzaldoximes, it is advisable, after adding the oxime and the alkyl halogen compound, to heat immediately at 50—60° for 15 to 30 minutes, and then to proceed as usual. In one experiment carried out in this way, ethyl β-benzaldoxime was obtained as a bright yellow oil; when heated at 200° with hydriodic acid, it yielded ethylamine free from ammonia. F. S. K.

Benzaldoximes. By E. Beckmann (*Ber.*, **22**, 1588—1597).—In view of the fact that Auwers and Meyer's hypothesis concerning the isomerism of the three benzildioximes is considered by its authors to derive considerable support from the fact that all three yield the same oxidation-product on treatment with potassium ferricyanide (Abstr., 1888, 597; *Ber.*, **22**, 716), the author has examined the oxidation products of the two benzaldoximes, which can no longer be regarded as having the same plane formula (preceding Abstract), and finds these also to be identical. When α-benzaldoxime in dilute alkaline solution is oxidised in the cold with a dilute solution of potassium ferricyanide containing a few drops of alkali, azobenzenyl peroxide is precipitated, and the solution is found to contain dibenzenylazoxime (Günther, *Annalen*, **252**, 44), benzaldehyde, and benzoic acid. β-Benzaldoxime yields similar oxidation products under like conditions.

Azobenzenyl peroxide, CHPh:N·O·O·N:CHPh, is best obtained by oxidising α- or β-benzaldoxime, in ethereal solution, with the nitrous gases formed by the action of nitric acid (sp. gr. = 1·4) on arsenic trioxide; the yield amounts to about 50 per cent. of that theoretically possible. It crystallises from a mixture of alcohol and chloroform in well-defined microscopic rectangles, melts at 105°, and is insoluble in alkali, almost insoluble in water, alcohol, and ether, and sparingly soluble in acetic acid, benzene, phenol, &c. On spontaneous evaporation of its solution in either benzene or chloroform, it is converted into dibenzenylazoxime. Reduction with alcoholic ammonium sulphide converts it into α-benzaldoxime, whilst further treatment in ethereal solution with nitrous fumes oxidises it to the compound  $\left.\begin{array}{l}\mathrm{CPh{:}N{\cdot}O}\\ \mathrm{CPh{:}N{\cdot}O}\end{array}\right>$; this crystallises from alcohol or acetic acid in broad, tetragonal needles, melts at 114—115°, evolves the odour of phenyl cyanate when further heated, and has a molecular weight of 232, as determined by Raoult's method in acetic acid solution.

When either α- or β-benzildioxime in ethereal solution is oxidised by means of nitrous fumes, a compound is obtained which crystallises in reddish-yellow forms, melts at 114—115°, and is not reduced by boiling with alcoholic ammonium sulphide or by heating with concentrated hydriodic acid at 100°. A second compound, melting at a temperature above 200°, is also produced in the oxidation, and after the reaction can be extracted from the ethereal solution by means of aqueous alkali. W. P. W.

Action of Potassium Hypobromite on Amides. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, 8, 173—201; compare Abstr., 1888, 1194).—The action of potassium hypobromite, or rather of a mixture of bromine and dilute potash, on benzenemetadisulphonamide, quinoline-orthosulphonamide, benzamide, and ortho-, meta-, and para-nitrobenzamide, is represented by the general equation $R\cdot CONH_2 + KOBr = R\cdot CONKBr + H_2O$.

When acetic acid is added to the potassium salt thus obtained, the bromamide ($R\cdot CONHBr$) is formed. This gives the potassium salt when dissolved in potash.

Benzenemetadisulphontetrabromamide, $C_6H_4(SO_2\cdot NBr_2)_2$. The potassium salt, $C_6H_4(SO_2\cdot NKBr)_2$, was prepared from the diamide, and on adding acetic acid to it, the dibromodiamide seemed to be formed, but split up immediately into the tetrabromodiamide and diamide, and a double salt was precipitated having the formula $C_6H_4(SO_2\cdot NBr_2)_2 + KBr + HBr$. This salt was also prepared by adding potassium bromide to a solution of the tetrabromodiamide in acetic acid. When heated, it gives off bromine; when it is treated with hydrobromic or hydriodic acid, the diamine is formed, and bromine or iodine is liberated. The tetrabromodiamine is obtained from this double salt by the addition of silver nitrate; it is separated from the silver bromide formed by means of acetic acid. Like all these bromamides it decomposes when heated, giving off bromine; it dissolves in potash, giving the potassium salt of the bromamide.

The barium salt of the tetrabromodiamide was prepared by treating the double salt mentioned above with barium acetate; it has the formula $(NBr_2\cdot SO_2\cdot C_6H_4\cdot SO_2\cdot NBr)_2Ba + 4H_2O$.

Quinoline-orthosulphonamide was prepared by treating the corresponding sulphonic acid with phosphorus pentachloride, and adding the sulphochloride thus obtained to ammonia; it melts at 184°. When treated with potash and bromine, it gives the potassium salt of *quinoline-orthosulphobromamide*, $C_9NH_6\cdot SO_2\cdot NHBr$, which is itself formed when the potassium salt is treated with acetic acid. This substance exhibits the characteristic reactions of bromamides; it decomposes on heating, and when it is dissolved in dilute alkali, and potassium iodide, and then hydrochloric acid added, iodine is liberated.

The barium salt was prepared by adding barium acetate to the potassium salt; it has the formula $(C_9H_6N\cdot SO_2\cdot NBr)_2Ba + 2H_2O$, and forms two kinds of crystals: in a cold solution, transparent needles, which probably contain more than 2 mols. of water of crystallisation; these are transformed at 30° into the other variety, which consists of shining crystals with many facets.

Benzoic bromamide, $C_6H_5\cdot CONHBr$, prepared by adding potash and bromine to benzamide, and then acidifying with acid; the solution must be cooled. The alkaline solution gives aniline when heated. Attempts to prepare the potassium salt were unsuccessful, an impure product being obtained.

Ortho-, meta-, and para-nitrobenzoic bromamides,

$$C_6H_4(NO_2)(CONHBr),$$

are all prepared by adding potash and bromine to the corresponding amides, and then adding acetic acid. They all decompose when heated; when they are treated with potash (and also when potassium hypobromite alone is added to the amides), the potassium salts are obtained; the meta- and para-salts are crystalline, the ortho-salt forms an oily liquid. With acetic acid, these give the bromamides; with potash, they give nitranilines, $C_6H_4(NO_2),CONKBr + 2KHO = KBr + K_2CO_3 + C_6H_4(NO_2){\cdot}NH_2$. These nitranilines may be obtained directly by heating the amides with potash and bromine.

When ortho- and meta- (and doubtless also para-) nitrobenzoic bromamides are treated with excess of dilute potash, salts are deposited, which have the formula $C_7H_7N_2O_5K$, and to which the authors assign the composition $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}COOK + H_2O$. These are decomposed by dilute acids, and nitranilines are formed.

C. F. B.

Compounds of the Benzyl Series. By A. HAFNER (*Chem. Centr.*, 1889, 671—672).—*Paranitrobenzylphthalimide,*

$$C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

melting at 172°, is prepared from potassium phthalimide and paranitrobenzenyl chloride. When heated with hydrochloric acid under pressure at 200°, it is decomposed, with formation of phthalic acid and *paranitrobenzylamine hydrochloride,* $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2,HCl$. The free amine is an oil; the platinochloride, nitrate, and picrate may be prepared. Tin and hydrochloric acid reduce it to *paramidobenzylamine. Paranitrobenzylacetoamide* melts at 133°; *paranitrobenzylbenzoylamide* melts at 155—156°; *paranitrobenzylcarbamide,* prepared from the hydrochloride and argentic cyanate, melts at 196—197°, with decomposition. With carbon bisulphide, paranitrobenzylamine forms the *dithiocarbamate*

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}SH,NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

melting at 193°. The thiocarbamide could not be prepared, but with alcohol the dithiocarbamate gave *paradinitrodibenzylthiocarbamide,* $CS(NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, from which, by the action of mercuric oxide on the alcoholic solution, *paradinitrodibenzyl carbamide,*

$$CO(NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2,$$

melting at 234° with decomposition, is prepared.

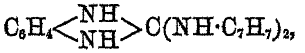
Ethyl paranitrobenzylcarbamate, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}COOEt$, is prepared from the amine by the action of ethyl chlorocarbonate; it melts at 116—117°.

Para-amidobenzylphthalimidine, $C_{15}H_{14}N_2O$, is prepared by reducing paranitrobenzylphthalimide with tin and hydrochloric acid; it melts at 187—188°. It forms a variety of salts with the halogen acids;

the picrate decomposes at 190°; the stannochloride melts at 183°. *Acetyl para-amidobenzylphthalimidine*, $C_8H_6O:N\cdot C_7H_6\cdot NHAc$, melts at 226—227°. Sodium nitrite converts the amidine into *parahydroxybenzylphthalimidine*, $C_8H_6O:N\cdot CH_2\cdot C_6H_4\cdot OH$. It forms red needles, melting at 189—198°. With tin and hydrochloric acid, the last-named substance yields a base, the *platinochloride* of which possesses the formula $(C_8H_9NO_2)_2,H_2PtCl_6$, and melts at 225°. J. W. L.

Condensation-products from Aromatic Carbodiimides and Orthodiamines. By I. Moore (*Ber.*, 22, 1635—1642; compare Dahm and Gasiorowski, Abstr., 1887, 247).—*Diphenylamidomethylenorthophenylenediamine*, $C_6H_4{<}{\scriptstyle NH \atop NH}{>}C(NHPh)_2$, is prepared by heating carbodiphenylimide and orthophenylenediamine in molecular proportion at 130—140° for four hours; after extracting it from the melt by means of benzene, it can be purified by distillation. It crystallises from benzene in tufts of small, hexagonal tables, melts at 159—160°, boils at a temperature above 400°, and is almost insoluble in water and light petroleum, sparingly soluble in ether, but readily in hot alcohol and benzene. The *hydrochloride*, $2C_{19}H_{18}N_4,3HCl$, crystallises in slender needles, and is readily soluble in alcohol and water; the *platinochloride*, $4C_{19}H_{18}N_4,3H_2PtCl_6 + (?)\ 6H_2O$, forms small, prismatic, orange-yellow needles; the *sulphate*, $C_{19}H_{18}N_4,H_2SO_4$, crystallises in slender, white needles, and is almost insoluble in cold water, readily soluble in hot benzene and alcohol. The *dibenzoyl*-derivative, $C_{19}H_{16}N_4Bz_2$, formed by heating the tetramine with five times its weight of benzoic anhydride at 130—140° for 1½ hours, crystallises in small, white tables, melts at 164—165°, and is very sparingly soluble in ether and light petroleum, sparingly soluble in benzene and cold alcohol. The *tetrabenzoyl*-derivative, $C_{19}H_{14}N_4Bz_4$, prepared by heating the tetramine with nine times its weight of benzoic anhydride at 220° for an hour, crystallises in small, granular or prismatic, white forms, melts at 147—148°, and is readily soluble in benzene, alcohol, and warm ether.

Diparatolylamidomethylenorthophenylenediamine,



$$C_6H_4{<}{\scriptstyle NH \atop NH}{>}C(NH\cdot C_7H_7)_2,$$

is formed under like conditions from carbodiparatolylimide and orthophenylenediamine, and crystallises from benzene in white needles or slender prisms, melts at 186—187°, distils at a temperature above 400° without decomposition, and is almost insoluble in light petroleum, readily soluble in hot alcohol and benzene. The *hydrochloride*, $2C_{21}H_{22}N_4,3HCl$, crystallises in lustrous, white needles and is readily soluble in water and alcohol; the *platinochloride*, $4C_{21}H_{22}N_4,3H_2PtCl_6 + 8H_2O$, is a reddish-yellow, microcrystalline powder; the *sulphate*, $C_{21}H_{22}N_4,H_2SO_4$, crystallises in needles, and is sparingly soluble in cold water. W. P. W.

Benzaldehyde. By A. Pinner (*Ber.*, 22, 1598—1600).—*Benzalimide*, $C_{42}H_{37}N_3O_2$, is formed when benzaldehyde is boiled for

4—6 hours in a reflux apparatus with about twice its weight of ammonium acetate, obtained by neutralising acetic acid with alcoholic ammonia. It crystallises in small prisms, melts at 247°, is very sparingly soluble in hot alcohol, acetic acid, benzene, acetone, &c., and yields an *acetyl*-compound, $C_{42}H_{36}N_3O_2Ac$, which crystallises in small prisms, melts at 178°, and is sparingly soluble in hot alcohol, readily soluble in hot acetone.

Instead of benzalimide, a compound was obtained in one experiment which on analysis gave figures agreeing fairly well with those required for the acetyl-derivative of benzylidenimide, $CHPh\colon NAc$. It melted above 300°, and, like benzalimide, was sparingly soluble in the ordinary solvents.

W. P. W.

Synthesis of Indene-derivatives. By W. v. MILLER and G. ROHDE (*Ber.*, **22**, 1830—1843).—*Chloromethylindene*, $C_{10}H_9Cl$, is obtained by diazotising amidomethylindene hydrochloride (Abstr., 1886, 701, 799) and adding the diazo-compound to a solution of cuprous chloride heated to 90°. It is an oil boiling at about 240° under a pressure of 720 mm., and dissolves in concentrated sulphuric acid with a dull rose-red colour. On oxidation with dilute nitric acid (1 part of acid containing 64·5 per cent. of nitric acid and 2 parts of water), it yields 1 : 2 : 4 chlorophthalic acid.

Metanitro-α-ethylcinnamaldehyde, $NO_2{\cdot}C_6H_4{\cdot}CH\colon CEt{\cdot}COH$, prepared by the condensation of metanitrobenzaldehyde and butaldehyde under conditions already described (Abstr., 1886, 560), crystallises from alcohol in tufts or concentric groups of small, narrow, rectangular scales, melts at 46°, can be distilled with steam, and is insoluble in water, soluble in alcohol and light petroleum, and readily soluble in ether, acetone, chloroform, and benzene. It reduces ammoniacal silver solution, forms a crystalline compound with sodium hydrogen sulphite, and yields a *hydrazone* crystallising in red needles melting at 135°. When metanitro-α-ethylcinnamaldehyde is reduced with tin and hydrochloric acid, it undergoes condensation with the production of *amidoethylindene*, $C_{11}H_{13}N$; this crystallises in large, feebly lustrous scales, melts at 89°, has a characteristic odour, and is insoluble in cold water, readily soluble in alcohol and ether. Of the salts of this base, the hydrochloride and sulphate are distinguished by their sparing solubility in cold water.

Metanitro-α-isopropylcinnamaldehyde, formed in like manner from metanitrobenzaldehyde and isovaleraldehyde, could not be obtained pure, but when freed as far as possible from oily condensation products it can be reduced with tin and hydrochloric acid, and yields *amidoisopropylindene*, $C_{12}H_{15}N$. This crystallises in scales, melts at 84°, and forms well-characterised salts.

W. P. W.

Action of Phosphorus Pentachloride on Acetophenone. By A. BÉHAL (*Bull. Soc. Chim.*, **50**, 632—635).—When the product of the action of phosphorus pentachloride on acetophenone is poured on a quantity of ice sufficient to decompose the phosphorus oxychloride formed, the solution produced deposits, after standing, a light, flocculent precipitate of the composition $COPh{\cdot}CCl_2{\cdot}PO(OH)_2$.

This substance is almost insoluble in benzene and chloroform, fairly soluble in ether, and dissolves readily in alcohol or in boiling water, crystallising from the latter in silky tufts and in very fine needles which melt at 152—153°, and decompose at a higher temperature into phosphoric acid and dichloracetophenone. It is a bibasic acid, reddening litmus, decomposing carbonates, and forming a crystalline calcium salt; fuming nitric acid is almost without action on it.

T. G. N.

Halogen-derivatives of Toluene and of Benzoic Acid. By C. WILLGERODT and H. SALZMANN (*J. pr. Chem.* [2], 39, 465—484).—The products of the action of chlorine on bromtoluenes, and of bromine on chlortoluenes were studied, these products then being converted into the corresponding derivatives of benzoic acid, in order to obtain some knowledge of their structure.

The chlorination or bromination takes place easily and rapidly in the presence of metallic iron, and the use of this substance is advised for such purposes.

As regards the oxidation to benzoic acid derivatives, it was found that neither dichromate and sulphuric acid, nor chromic acid and acetic acid could be used, as both of these mixtures caused a complete oxidation.

A dilute neutral solution of potassium permanganate gave the desired result, but the time required was considerable. The method finally adopted was to heat the substance to 150—200° for 8—10 hours in a sealed tube, with four or five times its weight of 20 per cent. nitric acid.

The general plan is as follows. A chlortoluene is treated with bromine, or a bromtoluene with chlorine, and the resulting product purified as far as possible by distillation. This product, generally a mixture, is oxidised to the corresponding derivatives of benzoic acid; these are converted into the barium salts, which are then separated by fractional crystallisation. From the barium salt, the silver, copper, and iron salts were prepared, and finally, from all of these the acid was set free by treatment with hydrochloric acid.

By this means four different chlorobromobenzoic acids were obtained, namely:—(1.) Metachloroparabromobenzoic acid, [Br : Cl : COOH = 4 : 3 : 1], melting at 170°, known to have this formula because it is prepared from parabromotoluene, which can only give rise to this acid, and (2) below. The barium salt crystallises in warty aggregates, the silver salt in well-marked needles. (2.) The 4 : 2 : 1-acid melting at 156°, prepared from both parabromo- and orthochlorotoluene. The barium salt crystallises with $3H_2O$ in nodular masses; the silver salt also in spherical aggregates. The 6 : 2 : 1-acid, melting at 132°, prepared from orthochloro- and orthobromotoluene. The barium salt crystallises in needles with 1 mol. H_2O. (4.) The 2 : 4 : 1-acid, melting at 217°, prepared from both orthobromo- and parachloro-toluene. The barium salt crystallises in small needles with $4H_2O$. Of these four acids, Claus and Pfeifer (*Ber.*, 5, 656) have previously prepared three, namely:—(1), (2), and probably (4).

From the method of preparation of these acids, the following conclusions are drawn. Parabromotoluene, when chlorinated, gives meta- and ortho-chloro-derivatives (the former in larger quantity), and finally acids (2) and (1). Orthochlorotoluene, when brominated, gives para- and ortho-bromo-derivatives, and finally acids (2) and (3). Orthobromotoluene, when chlorinated, gives para- and orthochloro-derivatives, and finally acids (4) and (3). Parachlorotoluene, when brominated, gives orthobromo- and other derivatives, and finally (4) and other acids.

If the mixture of ortho- and meta-chloroparabromotoluene is dissolved in nitric acid, and the solution poured into water, a considerable quantity of a solid mononitro-derivative of metachloroparabromotoluene melting at 61° is obtained, and also a small quantity of a liquid which probably contains mononitro-orthochloroparabromotoluene.

A mixture of bromorthochlortoluenes treated in a similar manner gave a solid nitrobromorthochlorotoluene melting at 68°, and also a liquid compound.

By partial sulphonation of the mixture of chloroparabromotoluenes, two sulphonic acids were obtained, and the residue gave on oxidation large quantities of orthochloroparabromobenzoic acid.

A solid dichloroparabromotoluene, melting at 87°, was obtained by the continued action of chlorine on parabromotoluene. It dissolves in nitric acid, forming a mononitro-derivative which melts at 106°, and on oxidation it is converted into a dichloroparabromobenzoic acid melting at 168°. The barium salt of this acid crystallises in slender needles with 3 mols. of water, and is soluble in hot water, but not easily in cold. The silver salt forms rosette-shaped masses of needles.

The dichlorobromotoluene has probably the formula $C_6H_2MeClBrCl = 1 : 2 : 4 : 5$, for it is obtained from both ortho- and meta-chloroparabromotoluene, and on treatment with sodium and methyl iodide a small quantity of symmetrical tetramethylbenzene was obtained.

Dibromorthochlorotoluene was obtained by the action of the requisite quantity of bromine on orthochlorotoluene; it melts at 100°, and has the formula $C_6H_2MeClBrBr = 1 : 2 : 4 : 6$, since it is obtained from both ortho- and para-bromorthochlorotoluene. Oxidised with nitric acid, it gives the corresponding benzoic acid, melting at 182°.

Trichloroparabromotoluene was obtained by the continued action of chlorine on parabromotoluene; it melts at 55—60°, and is possibly a mixture. It dissolves in nitric acid, giving a mononitro-derivative melting at 162°. The corresponding benzoic acid melts at 152°, and is but little soluble in water; its barium and silver salts were prepared.

Tetrachloroparabromotoluene was obtained by the chlorination of parabromotoluene; it melts at 213°. It is only with great difficulty oxidised to the corresponding benzoic acid; this melts at 198°, and is very little soluble in water. C. F. B.

Bromination of Orthacetylamidobenzoic Acid. By H. Alt (*Ber.*, **22**, 1643—1647).—In order to determine the position in the benzene molecule taken up by bromine when two substituents, the radicles COOH and NHAc, are already present in an ortho-position, the author has examined the bromo-derivative obtained by Jackson on brominating orthacetylamidobenzoic acid (Abstr., 1881, 735), and finds, as was to be expected, that it has the constitution [COOH : NHAc : Br = 1 : 2 : 5]. On hydrolysis, this bromorthacetylamidobenzoic acid yields an amido-acid, which melts at 211·5—212°, and gives an apple-green copper salt, but in other respects, such as the water of crystallisation of its salts, agrees with the 1 : 2 : 5-acid described by Hübner and Petermann (*Annalen*, **149**, 133). The lower melting point (208°) and light blue copper salt obtained by these authors from their acid must have been due to impurity, inasmuch as metabromorthacetoluidide, [Me : NHAc : Br = 1 : 2 : 5] (*Annalen*, **252**, 318), on oxidation with potassium permanganate and subsequent hydrolysis, is converted into an amido-acid identical with that obtained from Jackson's acid. W. P. W.

Bromotoluic Acids. By A. Claus and H. Kunath (*J. pr. Chem.* [2], **39**, 485—490).—Hitherto the constitutions of only three, or, at most, four, monobromotoluic acids were known with certainty, namely, Me : Br : COOH = 4 : 3 : 1; = 2 : 6 : 1; = 3 : 2 : 1; and = 3 : 4 : 1. The authors have now prepared the 4 : 2 : 1, 2 : 5 : 1, and 2 : 4 : 1 acids; the nitrile was prepared from the corresponding bromotoluidine by Sandmeyer's reaction, and converted into the acid by boiling with potash: the first reaction gave a yield of about 30 to 40 per cent. of the amine used; the second went quantitatively.

Orthobromoparatoluic Acid, [Me : Br : COOH = 4 : 2 : 1].—The bromotoluidine, prepared by brominating the acetyl-derivative of paratoluidine, boiled at 240°; the nitrile melts at 47°, is insoluble in water, soluble in alcohol, and volatilises with steam. The acid melts at 140°, and is soluble in water and alcohol. The ammonium, potassium (with 4 mols. H_2O), sodium (3 mols. H_2O), calcium (2 mols. H_2O), and barium (6 mols. H_2O) salts are soluble in water; the silver and lead salts form white, the copper a light-blue, precipitate.

Metabromoparatoluic acid, [Me : Br : COOH = 4 : 3 : 1], melting at 204°, was also prepared by the authors from the corresponding toluidine; the nitrile melts at 44°, and is soluble in alcohol and ether.

Metabromorthotoluic acid, [Me : Br : COOH = 2 : 5 : 1].—The nitrile melts at 42°, it is insoluble in water, soluble in alcohol and ether, and volatilises with water vapour. The acid melts at 118°, and is identical with that obtained by Claus and Pieszcek (Abstr., 1887, 240) by the oxidation of bromethyltoluene. It is soluble in alcohol, ether, and hot water, but not in cold water. The salts of the alkali metals are fairly soluble in water, those of barium and calcium are less soluble; whilst the copper salt forms a green, the silver and lead salts are white, precipitates.

Parabromorthotoluic acid, [Me : Br : COOH = 2 : 4 : 1], prepared also by Nourisson (Abstr., 1887, 668). The nitrile melts at 70°; the acid melts at 187°, and appears to be identical with that which Jacobson obtained (Abstr., 1884, 142) from the oxidation of bromortho-xylene, and to which he erroneously assigned the composition 5 : 2 : 1. The acid is but slightly soluble in water; the calcium salt is easily soluble, and crystallises, as Jacobson also found, with 2 mols. of water.

C. F. B.

Chloroparatoluic Acids. By A. Claus and N. Davidsen (*J. pr. Chem.* [2], **39**, 491—498).—The acids were prepared from their nitriles, which were prepared from the corresponding toluidines by Sandmeyer's reaction.

Orthochloroparatoluic acid, [Me : Cl : COOH = 4 : 2 : 1]. The nitrile melts at 61—62°; it is insoluble in water, but soluble in alcohol; when boiled with potash, it gives first the amide of orthochloroparatoluic acid (crystals of which are deposited when the boiling is stopped at the end of 1—2 hours), and finally, after continued boiling, the acid itself. The acid melts at 155°; it is soluble in water, alcohol, ether, &c., and it appears to be identical with the acid obtained by Fileti and Crosa (*Gazzetta*, **16**, 269) as a bye-product in the oxidation of chlorocymene. The ammonium, potassium, sodium (with 1 mol. H_2O), calcium (2 mols. H_2O), and barium (5 mols. H_2O) salts are very soluble in water; the silver salt is hardly soluble in alcohol and cold water, but easily in hot water, from which it crystallises out in brilliant anhydrous plates.

The amide, prepared as above described, is almost insoluble in water, but dissolves in hot alcohol; it melts at 182°. It can be boiled with water for hours without undergoing hydrolysis.

The action of nitric acid on orthochloroparatoluic acid gives one dinitro- and two mononitro-derivatives. After remaining for some time with cold fuming nitric acid, almost pure crystals of the acid NO_2 : Me : Cl : COOH = 5 : 4 : 2 : 1 separate; these melt at 180°, and dissolve in water and alcohol. From aqueous solutions, crystalline plates are deposited, from alcoholic solutions, slender prisms which afterwards change to the other form. The barium salt crystallises with 3 mols. H_2O; the ammonium salt is soluble in water.

The second mononitro-derivative was not obtained in sufficient quantity to furnish any trustworthy data. The dinitro-derivative, [COOH : Cl : Me : $(NO_2)_2$ = 1 : 2 : 4 : 3 : 5], melts at 233°, and dissolves in alcohol, but hardly at all in water. The barium salt crystallises with 3 mols. H_2O in large, brilliant prisms.

Metachloroparatoluic acid, [Me : Cl : COOH = 4 : 3 : 1], prepared like the orthochloro-compound, melts at 199°. The nitrile melts at 48°, and sublimes easily; it is soluble in alcohol. The amide dissolves both in hot water and in alcohol; when boiled with water, hardly any of it is converted into the acid; with potash, however, the conversion is complete. The ethyl ether was also prepared; it is a liquid boiling at 150°.

Nitro-derivatives of this acid are to be described in a later paper.

C. F. B.

Behaviour of Ammonia and Organic Bases with Sodium Phenoxyacrylate. By E. Erlenmeyer (*Ber.*, **22**, 1482—1483).—*Phenylamidolactic acid*, $NH_2 \cdot CHPh \cdot CH(OH) \cdot COOH$, is obtained when sodium phenoxyacrylate is dissolved in ammonia, the solution evaporated at the ordinary temperature, and the residue recrystallised from alcohol; it decomposes at 220—221°.

Phenylpiperidyllactic acid, $C_5NH_{10} \cdot CHPh \cdot CH(OH) \cdot COOH$, prepared by treating sodium phenoxyacrylate with piperidine in aqueous solution, decomposes at 244°.

Aniline also combines with sodium phenoxyacrylate, forming a crystalline additive compound, which is decomposed by hot acetic acid, yielding anilidolactic acid. F. S. K.

The Orthocoumaric and Orthocoumarinic Series. By W. v. MILLER and F. KINKELIN (*Ber.*, 22, 1705—1715).—*Orthonitrocoumarin*, [$NO_2 : OH : COH = 1 : 2 : 3$], was prepared from orthonitrosalicaldehyde by Perkin's reaction. It crystallises from benzene in prisms, from alcohol in needles, and melts at 191°. It dissolves in boiling dilute caustic soda or sodium carbonate, and the solution, when acidified, yields *orthonitrocoumarinic acid*, $C_9H_7NO_5$. This acid, which is the first *free* coumarinic acid obtained, is easily soluble in hot alcohol, from which it crystallises in long, yellow prisms. When heated quickly, it melts at 150° with evolution of water. It is easily soluble in dilute ammonia, and evolves carbonic anhydride when added to dilute sodium carbonate. When kept under water or alcohol, it is slowly reconverted into the anhydride, and this change is quickened by gentle heating. Its salts are easily prepared and are all explosive. The *basic sodium salt*, $C_9H_5NO_5Na_2$, forms red, hygroscopic prisms, sparingly soluble in absolute alcohol; the *barium salt*, $C_9H_5NO_5Ba + 3\frac{1}{2}H_2O$, crystallises in red needles; the *silver salt*, $C_9H_5NO_5Ag_2$, forms purple-red crystals. All attempts to obtain orthonitrocarbostyril from orthonitrocoumarin by heating it with alcoholic ammonia failed, brown decomposition products being formed.

The *dimethyl salt*, $C_{11}H_{11}NO_5$, was obtained by the action of methyl iodide on the silver salt. It is easily soluble in ether and hot alcohol, and crystallises in prisms melting at 69°. When heated with dilute caustic soda, it loses both methyl-groups, and is entirely converted into sodium orthonitrocoumarinate. Even an excess of dilute sodium carbonate effects this remarkable separation of the methoxy methyl, but if an excess of the methyl salt is used, the resulting product is a mixture of orthonitrocoumarinic acid and the *monomethyl ether*, $C_{10}H_9NO_5$. This is easily soluble in alcohol, crystallises in plates, and melts at 135—136°. It is readily converted into orthonitrocoumarinic acid by dilute alkali or alkaline carbonate.

With a view to compare the behaviour of the corresponding coumaric-derivatives, the silver salt of nitrosalicaldehyde was treated with methyl iodide. The *orthonitromethoxybenzaldehyde* thus obtained crystallises in yellow needles melting at 102°. It was then converted by Perkin's reaction into *orthonitromethylcoumaric* (*orthonitromethoxycinnamic*) *acid*, $C_{10}H_9NO_5$, which forms yellow needles, soluble in boiling alcohol and melting at 193°. The silver salt of this acid, when treated with methyl iodide, yielded the *dimethyl salt*, $C_{11}H_{11}NO_5$. This crystallises from boiling alcohol in needles, and melts at 88—89°. When treated with dilute alkalis, this substance undergoes the normal decomposition, losing its carboxylic methyl group, and it is only when long-continued treatment with strong, boiling, alcoholic soda is resorted to that the methoxy-methyl group is separated. *Orthonitrocoumaric acid*, $C_9H_7NO_5$, is readily soluble in boiling alcohol, forms yellow crystals, and melts with decomposition at 241—242°. Neither when heated with water or alcohol, nor even with aqueous hydrobromic acid saturated at 0°, does this acid yield a lactone like its isomeride.

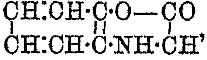
When methyl orthonitromethylcoumarinate is heated with dilute alcoholic ammonia at 100°, it is mainly converted into the ammonium orthonitrocoumarinate, but when heated for four hours at 150—160° with alcoholic ammonia saturated at 0°, *nitramidocinnamide*, $NO_2{\cdot}C_6H_3(NH_2){\cdot}CH{:}CH{\cdot}CONH_2$, is formed. This amide, when heated with aqueous hydrochloric acid at 130—140°, yields ammonia and *orthonitrocarbostyril*. The latter is easily soluble in alcohol and boiling water, crystallises in yellow prisms, and melts at 168°. It is easily soluble in mineral acids and dilute alkalis. Its *platinochloride* crystallises in minute needles. It is not identical with either of the three nitrocarbostyrils described (Abstr., 1885, 1139) by Friedländer and Lazarus.

These results show that there are two isomeric nitrohydroxycinnamic acids [$NO_2 : OH : CH = 1 : 2 : 3$]. Attempts made by v. Klobukow to determine their molecular weights showed these to be identical, so that the isomerism seems to be similar to that of the coumaric and coumarinic series generally.

During these researches the authors have noticed that the coumaric acids are very unstable towards acids. Their behaviour in this respect is under examination. L. T. T.

Transition from the Coumaric to the Quinoline Series.

By W. v. Miller and F. Kinkelin (*Ber.*, **22**, 1716—1718).—Although the authors were unable to pass from the coumaric to the quinoline series with orthonitrocoumaric or orthonitrocoumarinic acids, they have effected this transition with *nitromethoxycinnamaldehyde*, $C_{10}H_9NO_4$. This was prepared from orthonitrocoumaraldehyde (Abstr., 1887, 939) of m. p. 133°. It crystallises from alcohol in yellow prisms which melt at 115°. When oxidised with silver oxide, it yields orthonitromethylcoumaric acid (see preceding Abstract), and therefore belongs to the coumaric series. When heated with alcoholic ammonia at 130—140° for 3—4 hours, orthonitroquinoline (together with much resinous matter) is obtained. The reaction evidently takes place in two stages, as in the cold an ammonia additive compound is formed.

The authors have subjected the compound 

$$\begin{array}{l} CH{:}CH{\cdot}C{\cdot}O{—}CO \\ \;| \qquad\quad \| \qquad\quad | \\ CH{:}CH{\cdot}C{\cdot}NH{\cdot}CH \end{array}$$

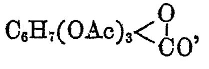
, described by Fritsche (*Jahresb. f. pr. Chem.*, 1879, 288), to the action of zinc-dust, and have obtained a very feebly basic substance boiling at 190—210°, which is under investigation. L. T. T.

Synthesis of Phenylpyruvic Acid.

By E. Erlenmeyer (*Ber.*, **22**, 1483—1484).—*Ethyl phenylcyanopyruvate*, $CN{\cdot}CHPh{\cdot}CO{\cdot}COOEt$, is formed when benzyl cyanide is treated with ethyl oxalate and sodium or sodium ethoxide, and the resulting ethyl sodophenylcyanopyruvate decomposed with acids. It crystallises in rectangular plates, melts at 129—130°, and alcoholic solutions give a green coloration with ferric chloride. It dissolves unchanged in cold alkalis and alkaline carbonates, but, when the alkaline solutions are warmed or kept for a long time, it is decomposed into benzyl cyanide and oxalic acid. When boiled with dilute sulphuric acid (1 : 10), carbonic anhydride is evolved and phenylpyruvic acid (compare Wislicenus, Abstr., 1887, 587), melting at 153—155°, separates on cooling in small, rhombic, or hexagonal plates.

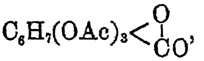
Quinaldine reacts with ethyl oxalate in the same way as benzyl cyanide. F. S. K.

Acetyl-derivatives of Quinic Acid. By E. Erwig and W. Koenigs (*Ber.*, **22**, 1457—1464).—*Triacetylquinide*,



$$C_6H_7(OAc)_3<\begin{array}{l}O\\ |\\ CO\end{array},$$

can be obtained by boiling quinic acid (10 grams) with acetic anhydride (70 c.c.) for several hours. The yield of the pure substance is 8 grams. It separates from hot water or alcohol in colourless crystals, melts at 132°, and is only sparingly soluble in cold water, alcohol, and ether, and almost insoluble in carbon bisulphide and sodium carbonate. Molecular weight determinations by Raoult's method in glacial acetic acid solution gave 298 as the average of three experiments. The formation of triacetylquinide may be employed for the identification of small quantities of quinic acid.

Isotriacetylquinide,  $C_6H_7(OAc)_3<\begin{array}{l}O\\ |\\ CO\end{array}$, is formed when quinic acid is heated with acetic anhydride (10 parts), first at 170° for some time, and then at 240—250°; it is also obtained when triacetylquinide (m. p. 132°) is heated with acetic anhydride at 240° for some hours. The yield of pure substance is 50 per cent. of the quinic acid employed. It crystallises from boiling alcohol, melts at 139°, and resembles the preceding compound in its behaviour towards solvents. Molecular weight determinations gave results in accordance with the above formula.

Tetracetylquinic acid, $C_6H_7(OAc)_4{\cdot}COOH$, can be prepared by treating quinic acid (5 grams) with acetic anhydride and a trace of zinc chloride, and, as soon as the first energetic reaction is at an end, boiling the mixture for 10—15 minutes. The resulting solution is evaporated to dryness, the residue mixed with water, shaken with ether, and the washed ethereal extract agitated with sodium carbonate solution; the alkaline solution is separated, acidified with dilute sulphuric acid, extracted with ether, and the ethereal solution washed, dried, and evaporated. Tetracetylquinic acid remains as a syrup, but gradually solidifies to a colourless, crystalline mass, melting at about 130—136°. It is readily soluble in hot water and most ordinary solvents, but only sparingly in carbon bisulphide, and almost insoluble in light petroleum. The salts are readily soluble. The *silver* salt, $C_{15}H_{19}O_{10}Ag$, forms colourless, spear-shaped crystals, and is readily soluble in water and alcohol, but insoluble in ether; it quickly turns yellow on exposure to light. The ethyl salt, prepared by treating the silver salt with ethyl iodide in alcoholic solution, separates from hot water in colourless scales, melts at 135°, and is only moderately soluble in cold alcohol and ether. This salt is identical with the compound obtained from ethyl quinate by Fittig and Hillebrand (Abstr., 1879, 159).

When quinic acid (2 grams) is heated with acetic anhydride (15 grams) for 10 hours at 170°, triacetylquinide and tetracetylquinic acid are formed. Hesse's tetracetylquinide (Abstr., 1880, 317) is probably a mixture of these two compounds. F. S. K.

Orthosulphobenzoic Acid and its Derivatives. By I. REMSEN and A. R. L. DOHME (*Amer. Chem. J.*, **11**, 332—348).—This acid is best prepared by boiling commercial "saccharin" with dilute hydrochloric acid, when it is split up into acid ammonium orthosulphobenzoate and parasulphaminebenzoic acid; the latter, being insoluble, is filtered off; the acid ammonium salt is mixed with twice its weight of phosphorous pentachloride, the mixture washed, the heavy yellow oil boiled with water till decomposed, and the solution evaporated to dryness. It forms colourless orthorhombic crystals (with 4 mols. H_2O), very soluble in water, slightly hygroscopic, and melting at 68—69°; the anhydrous acid melts at 130°, at which temperature it partially sublimes as long needles containing 2 mols. H_2O.

Orthosulphobenzoic anhydride, $C_6H_4{<}\substack{CO \\ SO_2}{>}O$, obtained by heating the acid with phosphoric anhydride at 130°, forms transparent needles or rhombs melting at 128°.

The following salts are described together with their crystallographical forms: the *normal barium* salt (2 mols. H_2O), the *acid barium* salt ($4\frac{1}{2}$ mols. H_2O), the *normal calcium* salt (5 mols. H_2O), the *acid calcium* salt (6 mols. H_2O), the *normal ammonium* salt, the *normal potassium* salt (2 mols. H_2O), the *normal silver* salt, the *silver ammonium* salt, the *normal copper* salt ($3\frac{1}{2}$ mols. H_2O), and the *normal magnesium* salt (x mols. H_2O).

The *chloride*, $SO_2Cl{\cdot}C_6H_4{\cdot}COCl$, is a colourless insoluble oil, which crystallises from ether in long orthorhombic prisms melting at 73°.

The acid ethereal salts are made either by boiling the above chloride with the alcohol or by passing dry hydrogen chloride through solutions of the acid in the alcohol. The normal ethereal salts are made from the silver salts of the acid ethereal salts. The following are described: the *acid methyl* salt, the *barium methyl* salt, the *silver methyl* salt, the *acid ethyl* salt, the *barium ethyl* salt, the *dimethyl* salt, the *diethyl* salt, the *ethyl methyl* salt, and the *methyl ethyl* salt. When treated with water, the normal ethereal salts lose the alkyl-group which is combined with the sulphuric acid residue, leaving the acid ethereal salt.

The substance obtained by Brackett by treating benzoic sulphimide successively with phosphorous pentachloride and methyl alcohol (Abstr., 1888, 283) is *methyl orthosulphamine-benzoate*,

$$NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}COOMe.$$

Ethyl orthosulphamine-benzoate is identical with the ethereal salt described by Fahlberg and List (Abstr., 1887, 835). *Propyl orthosulphamine-benzoate* was also obtained.

Orthosulphamine-benzoic anilide, $NH_2{\cdot}SO_2{\cdot}C_6H_4{\cdot}CONHPh$, obtained by heating either benzoic sulphimide or the above methyl salt with aniline, forms short, white, crescent-shaped needles melting at 189°.

Orthosulphamine-benzoic orthotoluide,

$$NH_2\cdot SO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4Me,$$

obtained by using orthotoluidine instead of aniline, forms radiated white needles melting at 193°. The *paratoluide* forms short, white needles melting at 202°.

When benzoic sulphimide is heated with phosphorous pentachloride in a sealed tube at 160°, it is converted into orthochlorophenyl cyanide.

A. G. B.

Iodophenolsulphonic Acids: Iodoquinones. By F. KEHRMANN (*J. pr. Chem.* [2], **39**, 392—402; compare Abstr., 1888, 595, 841).—*Orthiodothymolparasulphonic acid,* [$OH : Pr : SO_3H : Me : I = 1 : 2 : 4 : 5 : 6$], is obtained as its primary potassium salt by acting on potassium thymolparasulphonate (1 mol.) with iodine (1 atom) and iodic acid. It forms crystals which are soluble in water, melt at 80° in their water of crystallisation, and decompose at 120°. The *potassium* salt (with 2 mols. H_2O), the *barium, silver,* and *copper* salts are described. By treating this sulphonic acid or its salts with strong nitric acid, dinitrothymol, [$OH : Pr : Me : (NO_2)_2 = 1 : 2 : 5 : 4 : 6$], is obtained.

Orthiodopropylmethylquinone, [$O_2 : Pr : Me : I = 1 : 4 : 2 : 5 : 6$], is obtained when a sulphuric acid solution of a salt of the above sulphonic acid is treated with chromic acid. It crystallises in brilliant yellowish-red prisms which melt at 61° and are soluble in the usual organic solvents. The corresponding *quinol,* obtained by reducing this quinone with stannous chloride, forms colourless prisms, melting at 74° and easily soluble in organic solvents.

Iodopropylmethylquinonemonoxime, [$O : Pr : NOH : Me : I = 1 : 2 : 4 : 5 : 6$], is formed when a solution of the above quinone in 75 per cent. alcohol is heated for two hours with an excess of hydroxylamine hydrochloride. It crystallises in long, yellow prisms and needles, soluble in alcohol and ether, insoluble in cold water; it melts and decomposes at 130°; its alkaline solution is reddish-yellow. The *sodium*-derivative forms insoluble, greenish-yellow laminæ; the *acetyl*-derivative crystallises in beautiful, golden-yellow needles, melting at 69—70°, and soluble in all organic solvents.

Iodoamidothymol, [$OH : Pr : NH_2 : Me : I = 1 : 2 : 4 : 5 : 6$], is obtained when the above oxime is treated with the calculated quantity of stannous chloride, as a stannochloride which crystallises in large, colourless prisms, turning violet after a time. The pure thymol was not obtained.

Metaiodomethylquinone, [$O_2 : Me : I = 1 : 4 : 2 : 6$], obtained as previously described (Abstr., 1888, 842), melts at 116—117°. When reduced with stannous chloride, it yields the corresponding *quinol,* which crystallises in soft, silky aggregates of needles, soluble in organic solvents, and melting at 110—111°. With hydroxylamine, it yields the *monoxime;* this crystallises in aggregates of short, yellow prisms, soluble in alcohol and ether, insoluble in water, and melting with decomposition at 156°.

When potassium metacresolparasulphonate (Abstr., 1888, 281) is iodated with 2 atoms of iodine, *potassium diiodometacresolparasulphonate* [$OH : I_2 : Me : SO_3H = 1 : 2 : 6 : 3 : 4$] is obtained; it forms brownish tabular crystals, soluble in hot water. The *barium* salt was obtained, and from this the free *acid*, which crystallises in small needles, easily soluble, and decomposing at 70°. When this acid is reduced with chromic acid, it yields *metadiiodomethylquinone* [$O_2 : I_2 : Me = 1 : 4 : 2 : 6 : 3$]; this crystallises in garnet-red laminæ, melts at 112—113°, sublimes with partial decomposition, and is easily soluble in organic solvents; it yields trinitrometacresol (m. p. 104—105°) when treated with cold concentrated nitric acid.

A. G. B.

Behaviour of Alkyl-halogen Compounds towards Ethyl Sodophenylsulphoneacetate. By R. OTTO and A. RÖSSING (*Ber.*, **22**, 1447—1453).—The authors treated ethyl phenylsulphoneacetate with sodium ethoxide and ethyl iodide exactly as described by Michael and Palmer (Abstr., 1885, 987), but the only product was methylphenylsulphone. They repeated the experiment under varied conditions, and also tried to prepare the allyl- and benzyl-derivatives which have been described by Michael and Palmer (*loc. cit.*), and Michael and Comey (Abstr., 1884, 319). As all the experiments were unsuccessful and only resulted in the production of methylphenylsulphone, the authors leave the matter to be explained by Michael, Comey, and Palmer.

F. S. K.

Short Communications. By R. OTTO and A. RÖSSING (*Ber.*, **22**, 1453—1455).—When ethyl sodophenylsulphoneacetate is heated, a thick oil distils and the residue consists of tarry matters, sodium sulphide and sodium carbonate. The oily distillate contains phenyl mercaptan, phenyl sulphide, ethyl phenyl sulphide, and methylphenylsulphone. The decomposition product (m. p. 85°) described by Michael and Comey (Abstr., 1884, 319) is impure methylphenylsulphone.

When sodium benzenesulphinate (2 mols.) is boiled with sodium dibromhydrocinnamate (1 mol.) in alcoholic solution for four days, α-bromocinnamene, cinnamic acid, and other products are formed, but diphenylsulphonehydrocinnamic acid is not obtained.

F. S. K.

Action of Sulphuric Acid on Symmetrical Bromopseudocumene. By O. JACOBSEN (*Ber.*, **22**, 1580—1586).—When finely powdered symmetrical bromopseudocumene [$Me_3 : Br = 1 : 3 : 4 : 6$] is gradually added to about five times its weight of slightly fuming sulphuric acid at a temperature not exceeding 20—25°, and the solution allowed to remain at this temperature, sulphonation slowly ensues and is complete at the end of four weeks. A mixture of two sulphonic acids in approximately equal proportions is obtained, but these are derivatives not of the symmetrical but of the consecutive [$Me_3 : Br = 1 : 3 : 4 : 2$] bromopseudocumene: isomeric change having taken place during the sulphonation. In addition to these acids, a very small proportion of tribromopseudocumene was also formed, together with a similar amount of a compound which crystallised in compact, prismatic forms, melted between 215° and 235°, and gave on analysis figures pointing to the formula $C_{18}H_{19}Br_3$, but no trace of a sulphonic acid of symmetrical bromopseudocumene could be detected. The mixed sulphonic acids can be separated by repeated fractional crystallisation of the calcium and then of the sodium salts, and the latter further purified by crystallisation from large quantities of alcohol. The corresponding salts of the two acids, however, so closely resemble one another that it is impossible to determine their purity except by reducing them to the corresponding pseudocumenesulphonates which are well-characterised and can readily be separated when mixed. The salts of *bromopseudocumenesulphonic acid*, [$Me_3 : Br : SO_3H = 1 : 3 : 4 : 2 : 6$], are as a rule sparingly soluble in cold water; the *sodium* salt, with 1 mol. H_2O, crystallises from its concentrated aqueous solution in small, flat prisms or needles and from a dilute solution in well-formed tetragonal or hexagonal scales; the *potassium* salt, with 1 mol. H_2O, forms rhombic or hexagonal scales or tables; the *ammonium* salt crystallises in small, anhydrous, hexagonal scales or tables; the *calcium* salt, with 3 mols. H_2O, crystallises in long, flat prisms; the *barium* salt crystallises in arborescent groups of small needles or prisms; the *magnesium* salt, with 2 mols. H_2O, forms rhombic or hexagonal scales; the *amide* crystallises from alcohol in long, spear-like needles and melts at 185°. The salts of *bromopseudocumenesulphonic acid*, [$Me_3 : Br : SO_3H = 1 : 3 : 4 : 2 : 5$], are, as a rule, somewhat more soluble in water than those of the isomeric acid; the *barium* salt crystallises in small, compact, rhombic tables, and the *magnesium* salt, with 4 mols. H_2O, crystallises in long, hair-like needles, but with these exceptions the salts of this acid resemble those of its isomeride in crystalline form and contain like amounts of water of crystallisation, whilst the *amide* also resembles its isomeride in appearance and solubility, but melts at 194·5°. W. P. W.

Action of Sulphuric Acid on Symmetrical Iodopseudocumene. By C. KÜRZEL (*Ber.*, 22, 1586—1588).—The solution obtained by shaking symmetrical iodopseudocumene, [$Me_3 : I = 1 : 3 : 4 : 6$], with concentrated sulphuric acid at the ordinary temperature becomes dark in colour when allowed to remain for some time, and deposits a semi-fluid mass which when separated, washed with water, and distilled in a vacuum, is found to consist of two di-iodopseudocumenes. Of these, one crystallises from alcohol in colourless, compact, rhombic tables, melts at 73°, and cannot be distilled without decomposition except in a vacuum, whilst its isomeride which is formed in smaller quantity is a colourless oil, and does not solidify unless cooled in a freezing mixture. Pseudocumenesulphonic acid, [$M_3 : SO_3H = 1 : 3 : 4 : 6$], and an iodopseudocumenesulphonic acid are also formed in the reaction, and can be separated from the excess of sulphuric acid in the ordinary way. The *iodopseudocumenesulphonic acid* crystallises in nacreous scales, is sparingly soluble in dilute sulphuric acid, and yields salts sparingly soluble in water; the *barium* salt, with 1 mol. H_2O, crystallises in flat needles; the *sodium* salt, with 1 mol. H_2O, crystallises in scales. When the acid is hydrolysed with concentrated hydrochloric acid, a considerable separation of iodine occurs, and on this account it was not found possible to determine whether it is a sulphonic acid of symmetrical iodopseudocumene, or whether an isomeric change had taken place, analogous to that occurring in the case of the sulphonation of symmetrical bromopseudocumene (see preceding Abstract). W. P. W.

Synthesis of Isatoic Acid. By S. NIEMENTOWSKI and B. ROZANSKI (*Ber.*, 22, 1672—1677).—The authors have obtained isatoic acid by boiling anthranilic acid with excess of ethyl chlorocarbonate. Careful comparison was made with the acid prepared from isatin by Kolbe's method.

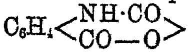
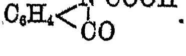
The reaction appears to take place in two stages, ethocarboxyanthranilic acid, $OEt\cdot CO\cdot NH\cdot C_6H_4\cdot COOH$, being first formed. This compound is formed, together with anthranilic acid hydrochloride, when anthranilic acid and ethyl chlorocarbonate in molecular proportion are mixed in ethereal solution in the cold. Both of these are converted into isatoic acid when heated with excess of ethyl chlorocarbonate, the hydrochloride passing first into the ethocarboxyl compound. The reactions are expressed by the equations:—

$$\text{i. } 2NH_2\cdot C_6H_4\cdot COOH + Cl\cdot COOEt = COOEt\cdot NH\cdot C_6H_4\cdot COOH + COOH\cdot C_6H_4\cdot NH_2,HCl;$$

$$\text{ii. } COOH\cdot C_6H_4\cdot NH_2,HCl + Cl\cdot COOEt = 2HCl + COOEt\cdot NH\cdot C_6H_4\cdot COOH;$$

$$\text{iii. } COOEt\cdot NH\cdot C_6H_4\cdot COOH + Cl\cdot COOEt = HCl + CO(OEt)_2 + C_8H_5NO_3.$$

Metahomoanthranilic acid in like manner yields *metabromisatoic acid*, $C_9H_7NO_3$, which crystallises from alcohol in silky white needles, and melts with decomposition at 226°; slow sublimation begins at 125°. It is soluble in ethyl and amyl alcohols, very sparingly so in chloroform, benzene and ether. Towards acids and alkalis, it behaves like isatoic acid, yielding carbonic anhydride and metahomoanthranilic acid.

The authors point out that these reactions would seem to indicate  $C_6H_4<\begin{matrix}NH\cdot CO\\CO-O\end{matrix}>$ as possibly the formula for isatoic acid in place of Friedländer and Wleugel's formula,  $C_6H_4<\begin{matrix}N\cdot COOH\\ |\\CO\end{matrix}$. L. T. T.

A Quinol and Quinone of Ditolyl. By K. BRUNNER (*Monatsh.*, 10, 174—183).—Toluquinol (15 grams) was dissolved in warm acetic acid (48 c.c.), the solution was cooled with ice, manganese dioxide (12 grams) added, and then a well-cooled mixture of acetic acid (15 c.c.) and sulphuric acid (7·5 c.c.) very gradually run in. Ice and water were then added, and the bluish-grey precipitate collected, and boiled with 200 c.c. of alcohol. On cooling, the filtered dark-red alcoholic solution deposited black crystals having a green iridescence (weight equal to 12 per cent. of the quinone taken). When these crystals were warmed with acetic acid and zinc-dust, a colourless solution was formed, and this on cooling deposited yellow prisms of *tetrahydroxyditolyl*, $C_{14}H_{10}(OH)_4$. This compound is readily soluble in warm water, and melts with slight blackening at 202° (uncorr.). The solution in alkalis becomes coloured on exposure to the air. The acetyl-derivative, $C_{14}H_{10}O_4Ac_4$, of which a good yield is obtained by heating it with 10 times its weight of acetic anhydride, and twice its weight of dry sodium acetate in a sealed tube at 155—165°, crystallises from alcohol in interlaced masses of needles which melt at 135°. *Tetramethoxyditolyl*, $C_{14}H_{10}(OMe)_4$, crystallises in prisms or plates which melt at 129° (uncorr.), and sublime unchanged at a higher temperature. In the preparation of this compound, an imperfectly methylated product is produced simultaneously; this is soluble in alkalis and in ether, forms a soft reddish mass, and when oxidised by ferric chloride or chromic mixture is converted into Nietzki's dimethoxyditolylquinone, $C_{16}H_{16}O_4$, melting at 152° (uncorr.); so that the tetrahydroxyditolyl, the derivatives of which are described by Nietzki (Abstr., 1878, 868) must be identical with that prepared in the manner described above.

The quinhydrone of tetrahydroxyditolyl, $C_{14}H_{14}O_4,C_{14}H_{10}O_4$, is obtained in bluish-violet scales, melting at 217—220° (uncorr.), when tetrahydroxyditolyl (5 grams) is oxidised with a 15 per cent. solution (31·5 c.c.) of ferric chloride, and the precipitate, obtained on allowing the solution to remain for several hours, is crystallised from alcohol. When the oxidation is brought about by means of concentrated ferric chloride or by a strong solution of chromic acid, both tetrahydroxyditolyl and quinhydrone furnish *ditolyldiquinone*, $C_{14}H_{10}O_4$. This crystallises from alcohol in yellow or orange-coloured prisms or plates, melts at 163° when heated rapidly, and sublimes in part unchanged at a higher temperature. G. T. M.

Diphenoltrichlorethane and Paradihydroxystilbene. By K. Elbs and O. Hoermann (*J. pr. Chem.* [2], 39, 498—502).—Just as diphenyltrichlorethane and its homologues give stilbene when treated with zinc-dust and ammonia, so Ter Meer (*Ber.*, 7, 1201) found that diphenoltrichlorethane, $CCl_3 \cdot CH(C_6H_4 \cdot OH)_2$, when boiled with alcohol and zinc-dust, is reduced to a diphenylethylene, which, as the authors find, has not the formula $CH_2 \colon C(C_6H_4 \cdot OH)_2$, but is paradihydroxystilbene, $HO \cdot C_6H_4 \cdot CH \colon CH \cdot C_6H_4 \cdot OH$. Ter Meer was unable to oxidise this substance; the authors, however, succeeded in oxidising the diacetyl-derivative with a solution of permanganate acidified with acetic acid; they obtained an acid which they identified with parahydroxybenzoic acid. Now, if the substance is asymmetrical diphenylethylene, $CH_2 \colon C(C_6H_4 \cdot OH)_2$, it should give on oxidation dihydroxybenzophenone, $CO(C_6H_4 \cdot OH)_2$, and finally 1 mol. of parahydroxybenzoic acid; if, on the other hand, it is paradihydroxystilbene, $HO \cdot C_6H_4 \cdot CH \colon CH \cdot C_6H_4 \cdot OH$, it should give 2 mols. of parahydroxybenzoic acid. It was found that, in spite of unavoidable loss, 6·0 grams of the diacetyl-derivative gave 3·3 grams of parahydroxybenzoic acid (calculated for 1 mol. 2·79, for 2 mols. 5·58 grams); hence the original compound must have had the symmetrical formula. Further, since nothing but parahydroxybenzoic acid was formed, both the hydroxyls in dihydroxystilbene must occupy the para-position. Still further proof is furnished by the authors, for they converted paranitrobenzyl chloride into dinitrostilbene; they reduced this to diamidostilbene, and then, by means of the diazo-reaction, replaced the amido-groups by hydroxyl. The melting point (280°) of the dihydroxystilbene thus obtained is precisely that of the substance obtained by reducing paradiphenyltrichlorethane. Moreover, the two diacetyl-derivatives agree in melting point (213°) and other properties. With diazosulphonic acids, parahydroxystilbene gives azo-colouring matters, though not very easily. When heated with ammonia, it is not acted on.

When paradihydroxydiphenylethane is dissolved in acetic acid and nitric acid added to the solution, a dinitro-derivative is obtained; if sulphuric acid also is added, a tetranitro-derivative is formed; these substances behave like acids, yielding salts; when quickly heated, they explode.

As regards the metallic derivatives of *dinitroparadihydroxydiphenyltrichlorethane*, $CCl_3{\cdot}CH[C_6H_3(NO_2){\cdot}OH]_2$, those with ammonium, sodium, and potassium are yellow and crystalline, and dissolve in water; the calcium-derivative forms a yellow, and the barium-derivative a cinnamon-coloured precipitate, insoluble in water. The *dinitro*-compound itself melts at 159°; with acetic anhydride it gives a diacetyl-compound soluble in acetic acid and in hot alcohol, and melting at 197°. When reduced, it gives a diamido-compound insoluble in water and chloroform, soluble in alcohol and ether; this compound when heated chars without melting; and, being both a phenol and an amine, dissolves in alkalis and acids.

The *tetranitro*-compound melts at 252°, and is slightly soluble in hot water and alcohol; the ammonium- and the sodium-derivatives are yellow, crystalline, and soluble; the potassium-derivative forms red, the calcium-derivative yellow, and the barium-derivative reddish-yellow crystals, little soluble in water; the copper-derivative is an insoluble, yellowish-green precipitate; the amide obtained by reduction is very unstable. The authors conclude by describing a convenient method for preparing paradiamidostilbene. C. F. B.

Conversion of Methylbenzylidene Chloride into Triphenylbenzene. By A. BÉHAL (*Bull. Soc. Chim.*, **50**, 635—638; compare p. 984).—After standing for eight months, the liquid product of the action of phosphorus pentachloride on acetophenone exploded, and at the same time crystals of triphenylbenzene were formed. In investigating this change, the author found that water determined the decomposition of the original substance into hydrogen chloride, monochlorocinnamene, and acetophenone, the latter compound resulting from the action of water on the first formed monochlorocinnamene. Monochlorocinnamene, when saturated with dry hydrogen chloride, and heated in a sealed vessel at 40°, exploded with formation of triphenylbenzene crystals. From these results, the author suggests that 3 mols. of monochlorocinnamene lose 3 mols. of hydrogen chloride, and yield 1 mol. of triphenylbenzene.

T. G. N.

Derivatives of Diphenylacetic Acid and of Benzilic Acid. By H. BICKEL (*Ber.*, **22**, 1537—1539).—*Ethyl diphenylchloracetate*, $CPh_2Cl{\cdot}COOEt$, prepared by treating diphenylacetic chloride with cold alcohol, or by the action of phosphoric chloride on ethyl benzilate, crystallises from chloroform in plates, melts at 43—44°, and is soluble in alcohol and ether.

Ethyl diphenylcyanoacetate, $CN{\cdot}CPh_2{\cdot}COOEt$, obtained by heating the preceding compound at 120—130° for 24 hours with mercuric cyanide, crystallises from alcohol in yellowish plates melting at 59°.

Ethyl tetraphenylsuccinate, $COOEt{\cdot}CPh_2{\cdot}CPh_2{\cdot}COOEt$, prepared by treating ethyl diphenylchloracetate with finely-divided silver at 120—130° for 12 hours, melts at 88—89°. The free *acid* melts at 260—262° with decomposition, and is readily soluble in alcohol and ether, but insoluble in water.

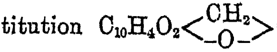
Diphenylacetic chloride, $CPh_2Cl{\cdot}COCl$, can be prepared by heating benzilic acid with phosphoric chloride (2 mols.) at 120—130°, pouring the product into cold water, and recrystallising the precipitate from light petroleum. (Compare Klinger and Standke, this vol. p. 885.) It forms large, colourless crystals, melts at 50°, and is not decomposed by cold, and only slowly by hot water. When heated with alcohol, it yields ethyl benzilate, and when treated with anhydrous ammonia in ethereal solution it is converted into diphenylchloracetamide; the last-named compound melts at 115°, and is converted into benzilamide by boiling water. Methyl and ethyl benzilates can be prepared by passing hydrogen chloride into a cold solution of benzilic acid in the corresponding alcohol. (Compare Klinger and Standke, *loc. cit.*) The products are oils, and do not crystallise readily unless agitated with a little of the crystalline salt prepared from silver benzilate.

Ethyl acetylbenzilate, $OAc{\cdot}CPh_2{\cdot}COOEt$, melts at 65°, the corresponding methyl salt at 122°; both compounds dissolve in concentrated sulphuric acid with an orange-yellow coloration, which changes to red on warming gently. F. S. K.

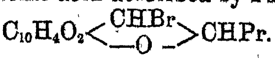
Fluoronaphthalenes. By A. EKBOM and R. MAUZELIUS (*Ber.*, **22**, 1846).—*α-Fluoronaphthalene*, $C_{10}H_7F$, is prepared by dissolving *α*-naphthylamine in warm, strong hydrofluoric acid contained in a platinum dish, and adding an excess of potassium nitrite in concentrated aqueous solution; the product is then neutralised with sodium carbonate, treated with aqueous soda to remove *α*-naphthol, and steam distilled. It is a colourless, refractive liquid, which boils at 212° under a pressure of 768 mm., has a sp. gr. = 1·135 at 0°, and is insoluble in water, readily soluble in alcohol, benzene, chloroform, and acetic acid.

β-Fluoronaphthalene, prepared in like manner from *β*-naphthylamine, crystallises in colourless, lustrous scales, melts at 59°, boils at 212·5° under a pressure of 760 mm., and resembles the *α*-compound in solubility. W. P. W.

Constitution of Lapachic Acid and its Derivatives. By S. HOOKER and W. H. GREENE (*Ber.*, **22**, 1723—1727).—Lapachic acid, a compound obtained from the Lapacho tree of South America, has been investigated by Paternò (Abstr., 1883, 210), who assigned to it the constitution $OH\cdot C_{10}H_4O_2\cdot CH{:}CHPr^{\beta}$, hydroxyamenylnaphthaquinone; he found that when treated with concentrated sulphuric acid it gives a red, crystalline substance (lapachone) to which he assigned the formula $C_{30}H_{28}O_6$.

The authors have obtained an orange-red substance, identical with lapachone, from South African Bethabana wood, and find that it gives many of the reactions characteristic of the quinones. With sodium hydrogen sulphite, it yields a colourless, crystalline compound, which is reconverted into the original substance by acids and alkalis; it combines very readily with hydroxylamine and with ammonia, and shows Bamberger's colour reaction for quinones. The molecular weight determinations by Raoult's method gave results agreeing with the molecular formula $C_{16}H_{14}O_3$. Lapachone has probably the constitution  $C_{10}H_4O_2<\genfrac{}{}{0pt}{}{CH_2}{-O-}>CHPr$, and is formed from lapachic acid by the addition and subsequent abstraction of 1 mol. of water under the influence of the acid; this view of its constitution agrees with all the known properties and reactions.

The compound $OH\cdot C_{10}H_{11}O_2\cdot CH_2\cdot CHPr\cdot OH$ is formed when lapachone is dissolved in boiling alkalis, and the cold solution neutralised with acetic acid. It separates from cold alcohol or acetic acid in large crystals, melts at 125°, is readily soluble in most ordinary solvents, and is readily reconverted into lapachone by dilute mineral acids. The *barium*-derivative crystallises in orange-red needles containing 1 mol. H_2O. The *silver*-derivative crystallises in dark, reddish brown needles with 1 mol. H_2O.

The bromolapachic acid described by Paternò (*loc. cit.*) probably has the constitution  $C_{10}H_4O_2<\genfrac{}{}{0pt}{}{CHBr}{-O-}>CHPr$.

F. S. K.

Hydrogenation of β-Diethylnaphthylamine. By E. BAMBERGER and S. WILLIAMSON (*Ber.*, 22, 1760—1764).—*β-Diethylnaphthylamine*, $C_{10}H_7\cdot NEt_2$, is a colourless, viscid oil, which boils without decomposition at 316° (thermometer in vapour) under a pressure of 717 mm., and very rapidly becomes brown on exposure to air. The *hydrochloride*, $C_{10}H_7NEt_2,HCl$, melts at 175°, is extremely soluble in water, and when distilled with lime decomposes into β-naphthylamine and butylene; the *platinochloride*, $(C_{14}H_{17}N)_2,H_2PtCl_6$, a bright-yellow crystalline powder, melts at 95°, and decomposes when its aqueous solution is boiled.

When β-diethylnaphthylamine is hydrogenated by the method already described, it yields a mixture of the "aromatic" and "alicyclic" bases, the former being the chief product (compare Bamberger and Schieffelin, this vol., p. 892); these can be separated in the usual way. *Ac. tetrahydro-β-diethylnaphthylamine* is an oil almost insoluble in aqueous soda, sparingly soluble in water, readily soluble in the ordinary organic solvents, and has all the properties of an "alicyclic" base. The *carbonate* crystallises in long, deliquescent needles, and the *hydrochloride* forms lustrous, thin prisms. *Ar. tetrahydro-β-diethylnaphthylamine*, $C_{10}H_{11}\cdot NEt_2$, is a colourless oil, which does not solidify in the cold, boils at 167° under a pressure of 16 mm., and at 298° under a pressure of 709 mm.; rapidly becomes brown on exposure to air, and is insoluble in aqueous soda, sparingly soluble in water, and readily soluble in the ordinary solvents. It shows all the properties of an "aromatic" tetrahydro-base, yields adipic acid on oxidation with potassium permanganate, and in combination with paradiazobenzenesulphonic acid forms a ponceau-red dye.

W. P. W.

Oxidation of β-Naphthol. By E. EHRLICH (*Monatsh.*, **10**, 115—122).—The author has previously (Abstr., 1888, 1306) described the preparation of orthocarboxycinnamic acid from β-naphthol, and has noted the simultaneous production of resinous matters, a dye, and a second crystalline acid formed to the extent of only about 2 per cent. This acid may be most conveniently prepared by slowly adding a solution of 200 grams of potassium permanganate, dissolved in 4 litres of water, to a well-cooled solution of 100 grams each of β-naphthol and potash in 3 litres of water. After standing for a short time, the product is filtered, the filtrate slightly acidified with sulphuric acid, again filtered from the coloured substance, the filtrate mixed with excess of dilute sulphuric acid, and, after 36 hours, the brown resinous deposit is collected, well washed with water, and dried in the air. The solution contains a large quantity of orthocarboxycinnamic acid, which may be extracted with ether. The dry resinous product is repeatedly extracted with boiling alcoholic ether, the solution concentrated, and the crystalline mass, which separates on cooling, is first washed with alcohol and then boiled with a little dilute alcohol to remove traces of orthocarboxycinnamic acid. The residue is dissolved in boiling alcohol, hot water added to the filtered solution, and the precipitate recrystallised from alcohol. The product thus obtained still contains traces of impurities, which may be removed by converting it into the barium salt and several times recrystallising. The pure acid is bibasic, forms colourless rhombic plates, melts at 281°, and has the composition $C_{20}H_{12}O_4$. It dissolves sparingly in benzene, chloroform, and light petroleum, is only very slightly in ether, alcohol, and acetic acid, and is insoluble in water. The ammonium salt is very unstable, the barium salt, $(C_{20}H_{11}O_4)_2Ba + 7H_2O$, crystallises from hot water in colourless plates, the silver salt is amorphous, and the ethyl salt, $C_{20}H_{11}EtO_4$, melts at 123—124°.

On reducing this acid with sodium amalgam, a new bibasic acid, $C_{20}H_{14}O_4$, is obtained. It crystallises in colourless plates, melting at 223—224°, and is probably related to the acid of the same molecular formula obtained by Henriquez (Abstr., 1888, 842) on oxidising α-naphthol with potassium permanganate. G. T. M.

1 : 4′-Fluoronaphthalenesulphonic Acid. By R. MAUZELIUS (*Ber.*, **22**, 1844—1845).—1 : 4′-*Fluoronaphthalenesulphonic acid* is obtained when α-diazonaphthalenesulphonic acid is dissolved in warm, 50 per cent. hydrofluoric acid; it crystallises in very soluble, small, lustrous scales, and forms salts which are not well characterised. The *chloride*, $C_{10}H_6F\cdot SO_2Cl$, crystallises in colourless, rhombic prisms, melts at 122—123°, and is sparingly soluble in light petroleum, readily soluble in benzene, hot acetic acid, and chloroform; the *bromide*, $C_{10}H_6F\cdot SO_2Br$, resembles the chloride in properties, and melts at 145°; the *amide*, $C_{10}H_6F\cdot SO_2NH_2$, forms sparingly soluble, lustrous scales, and melts at 196—197°; the *methyl* salt crystallises in colourless needles, and melts at 118°; the *ethyl* salt forms large prisms, and melts at 79°. It is noteworthy that with the exception of the amide, these derivatives melt at temperatures higher than the corresponding derivatives of the 1 : 4′ chloro-, bromo-, and iodo-acids.

W. P. W.

Camphor and Borneol of Rosemary; Separation of Camphor from Borneol. By A. HALLER (*Compt. rend.*, **108**, 1308—1310).—When essence of rosemary is distilled, the fraction boiling above 190° deposits on cooling a considerable quantity of a mixture of camphor and borneol, which may be purified by sublimation with calcium oxide.

The method of separation, which is applicable in all similar cases, is based on the fact that with bibasic acids camphols yield acid ethereal salts, which dissolve in alkaline liquids. The mixture was triturated with 0·6 times its weight of succinic acid, heated at 140° under pressure for 48 hours, and the cooled product treated with ether, which dissolves the camphor and the ethereal salt of the borneol, but leaves the excess of succinic acid undissolved. The ethereal solution is then agitated with a solution of sodium carbonate; the camphor remains in the ether, but the borneol salt passes into the aqueous solution. The latter is then treated with ether to remove traces of camphor, acidified, and again extracted with ether, which on evaporation leaves the acid borneol succinate. It is better, however, to boil the alkaline solution with soda, and then extract the borneol, which is liberated by saponification. It is purified by sublimation or by crystallisation from light petroleum.

Rosemary camphor contains about 5 per cent. of borneol, which forms hexagonal lamellæ, melting at 207·5°, and resembling those of ordinary borneol.

Measurements of the rotatory power and preparation of the monobromo-derivatives show that rosemary camphor is a mixture of dextrogyrate camphor and borneol with lævogyrate camphor and borneol.

C. H. B.

Acetates and Benzoates of Active and Racemic Camphols; Preparation of a Dextro-borneol Identical with Dryobalanops Borneol. By A. HALLER (*Compt. rend.*, **109**, 29—31).—The camphol is heated with glacial acetic acid at 200°, or with acetic anhydride at 100° for about three days, and the product washed and distilled. Both the dextrogyrate and lævogyrate acetates crystallise, but the racemic acetate formed by mixing them in equivalent proportions does not crystallise even at −17°. The active acetates boil at 225—226°, and the melted crystals very readily remain in superfusion.

Benzoates of camphols are obtained by heating with benzoic chlorides until evolution of hydrogen chloride ceases. The product is a colourless oil, which gradually crystallises at a winter temperature. Both the dextrogyrate and lævogyrate benzoates have the same appearance and an equal rotatory power (44°). When saponified, they yield camphol with the same rotatory power as the original camphol.

Racemic camphol benzoate forms a crystalline mass resembling the active benzoates.

The separation of the dextrogyrate and lævogyrate borneols obtained by the hydrogenation of camphor is effected more conveniently than by Montgolfier's method, by converting them into acetates, and crystallising the dextrogyrate acetate from the superfused mixture by adding a crystal of the solid salt. It is purified by crystallisation from light petroleum.

A borneol obtained by Baubigny's method had a rotatory power of +10°, and gave an acetate melting at 24°, with a rotatory power (+44° 58′) identical with that of the acetate of ordinary dextrogyrate borneol, and when this acetate was saponified it yielded ordinary borneol with a rotatory power $[\alpha]_D = +37° 63'$.

C. H. B.

Dibornylamine. By R. Leuckart and H. Lampe (*Ber.*, **22**, 1851—1853).—*Dibornylamine*, $(C_{10}H_{17})_2NH$, is formed in the preparation of bornylamine by the action of ammonium formate on camphor, and can be isolated by hydrolysing the crude product, and submitting the resulting mixture of amines to fractional distillation. 60 grams of camphor yield 30 grams of bornylamine and 2·25 grams of dibornylamine. It crystallises from alcohol in small plates, melts at 59—61°, boils at 342—344° (corr.), and has a slight odour both of camphor and piperidine. It is readily soluble in alcohol, ether, benzene, light petroleum, chloroform, and carbon bisulphide, the solutions having an alkaline reaction, but it is almost insoluble in water, and not so readily soluble in dilute acids as bornylamine. It does not absorb carbonic anhydride or moisture from the air, and the salts are less easily soluble in water than those of the primary base. The *hydrochloride*, $(C_{10}H_{17})_2NH,HCl$, is a colourless, crystalline compound, melting at about 250° with decomposition; it is readily soluble in alcohol, but only moderately so in water. The *platinochloride*, $[(C_{10}H_{17})_2NH]_2,H_2PtCl_6$, crystallises from hot, dilute alcohol in long, yellow needles, and is readily soluble in alcohol, but only sparingly in cold water. The *mercurochloride*, $(C_{10}H_{17})_2NH,HHgCl_3$, crystallises from dilute alcohol in colourless needles, melts at 192—195°, and is readily soluble in alcohol, but only sparingly in water. The *nitrate*, $(C_{10}H_{17})_2NH,HNO_3$, crystallises from hot water in silvery plates, and is only sparingly soluble in water, but readily in alcohol.

F. S. K.

Constituents of Herniaria. By L. Barth and J. Herzig (*Monatsh.*, **10**, 161—173).—An alcoholic extract of *Herniaria hirsuta*, a caryophyllaceous plant, contains *herniarin* (1 kilo. of the coarsely-powdered leaves yields 2 grams), a substance which, at ordinary temperatures, is odourless, but at 100° emits an odour of coumarin; melts at 117—118° (uncorr.), dissolves in concentrated sulphuric acid, forming a yellow solution with a bluish-white fluorescence, and in alkalis forming a yellow solution, from which it is again precipitated on neutralisation with an acid. It has the formula $C_{10}H_8O_3$, and is a methyl ether of umbelliferone, seemingly identical with that described by Tiemann and Reimer (Abstr., 1879, 720). When heated with alcoholic potash, it yields methylumbellic acid, $C_{10}H_{10}O_4$, a substance crystallising from water in small, glistening needles, which melt with decomposition at 180—185°.

The alcoholic extract of *herniaria* also contains a glycoside, which is precipitated by alcohol from an aqueous solution in the form of a greyish-white powder. It has the same toxicological action as commercial saponin, which it resembles in most of its properties; it differs from it, however, in giving a brown solution with concentrated sulphuric acid (saponin gives a violet solution), in the readiness with which it solidifies to a resinous mass when exposed to air and light, and in its yielding a sugar and a new compound when heated with hydrochloric acid at 140—150°. This new compound, $C_{14}H_{22}O_3$, is insoluble in water, and crystallises from acetic acid in needles which do not melt at 290°. The authors name the new compound *oxysapogenin*, as it contains one oxygen-atom more than sapogenin. Sapogenin melts at 256—260°. G. T. M.

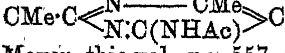
Brazilin. By C. SCHALL and C. DRALLE (*Ber.*, **22**, 1547—1564; compare this vol., p. 55).—Determinations of the molecular weight of brazilin tetramethyl ether by Raoult's method gave the molecule as $C_{16}H_{10}O(OMe)_4$.

Brazilin yields two series of bromo-derivatives, namely, (*a*) derivatives which do not lose bromine when treated with dilute ammonia, and (*b*) derivatives which lose part of their bromine when so treated.

Of class (*a*), the authors have obtained a monobromobrazilin differing from Buchka and Erk's; *dibromobrazilin*, $C_{16}H_{12}Br_2O_5 + 2H_2O$, soluble in water, crystallising in almost colourless scales and melting at 170—180°; and *tribromobrazilin*, almost insoluble in water, forming flesh-coloured crystals decomposing at 197—200°.

Of class (*b*) they have obtained tetrabromobrazilin, $C_{16}H_8Br_4O_5$ (?) in orange crystals; *hexabromobrazileïn*, $C_{16}H_6Br_6O_5$, previously described (*loc. cit.*) as pentabromobrazilin decomposing at 170—180°; *octobromobrazileïn*, decomposing at 130—140°; and *nonobromobrazilin*, $C_{16}H_5Br_9O_5$. The latter class of compounds (*b*), which have not been obtained free from acetic acid, probably are bromides of bromobrazileïns, or acetyl-derivatives of these.

From the mother-liquors of the oxidation product, $C_{20}H_{14}O_9$ (or more probably $C_{16}H_{10}O_7$), previously described (*loc. cit.*), the authors have obtained crystals which they believe to be orthoparadihydroxybenzoic acid (β-resorcylic acid). L. T. T.

Amidines and Pyrimidines. By A. PINNER (*Ber.*, **22**, 1600—1612).—The two compounds, anhydrodiacetylacetamidil, $C_8H_{11}N_3O$, and anhydrodiacetylacetamidine, $C_6H_8N_2O$, obtained by the action of sodium acetate and acetic anhydride on acetamidine hydrochloride (Abstr., 1884, 722), have been further examined, and the former proves to be the acetyl-derivative of amidodimethylpyrimidine,  $\mathrm{CMe{\cdot}C}\begin{array}{l}\nearrow \mathrm{N{-\!-\!-\!-}CMe}\searrow\\ \searrow \mathrm{N{:}C(NHAc)}\nearrow\end{array}\mathrm{CH}$, since it yields cyanmethine (comp. v. Meyer, this vol., pp. 557, 685) on hydrolysis with barium hydroxide. The best method of obtaining the acetyl-compound consists in heating acetamidine hydrochloride with an equivalent quantity of anhydrous sodium acetate and eight times the weight of acetic anhydride for 2 to 3 hours in a reflux apparatus, treating the cold solution with absolute alcohol, filtering from the separated sodium chloride, and distilling the filtrate to remove ethyl acetate; the acetyl-compound crystallises from the residual liquid in the retort on cooling. Anhydrodiacetylacetamidine is not formed in this reaction. When propionamidine hydrochloride is treated with acetic anhydride and sodium acetate under like conditions, a small proportion only of the pyrimidine-derivative, $C_8H_{13}N_3$ (*loc. cit.*) is obtained, the chief product being acetylpropionamide.

Benzoylbenzamidine, NH:CPh·NHBz, is formed when benzamidine hydrochloride, dissolved in dilute aqueous soda, is treated with benzoic anhydride. It crystallises from dilute alcohol in long prisms, melts at 105°, and when dissolved in hydrochloric acid is converted into dibenzamide. It is identical with Pinner and Klein's dibenzimide oxide obtained by the action of fuming sulphuric acid on benzonitrile (Abstr., 1878, 864; compare Gumpert, Abstr., 1885, 52).

Diphenylcarbamide is the product formed when a solution of benzamidine hydrochloride is treated first with phenyl cyanate and then with aqueous soda, but if the calculated quantity of aqueous soda is added to benzamidine hydrochloride in aqueous solution, and phenyl cyanate in less than the theoretical quantity is subsequently added in small portions at a time with vigorous shaking, *benzenyldiureïde*, NHPh·CO·NH·CPh:N·CO·NHPh, is obtained. This crystallises in slender, woolly needles, melts at 172°, is insoluble in water, and very sparingly soluble in alcohol; when dissolved in hot acetic acid, it is decomposed into *benzoylphenylcarbamide*, NHPh·CO·NHBz, and phenylcarbamide; the former crystallises in slender needles and melts at 195—200°. *Benzamidinethiocarbamide*, NHPh·CS·NH·CPh:NH, obtained by treating benzamidine hydrochloride with phenyl thiocarbimide, crystallises in lustrous, yellowish prisms, melts at 125°, and is more readily soluble in the ordinary solvents than the diureïde.

Amidines combine with diazo-compounds, thus *diazobenzenebenzamidine*, $NH:CPh·NH·N_2Ph$, is formed by adding a solution of diazobenzene chloride to benzamidine hydrochloride and precipitating with aqueous soda. It crystallises in lustrous, yellow prisms, melts at 181°, is slightly soluble in alcohol and benzene, more soluble in acetone; when boiled with water, it slowly decomposes with the production of phenol.

Benzamidine-chloral, $CPh(NH)NH_2,CCl_3·CHO$, obtained by adding the calculated quantity of chloral hydrate and potassium carbonate to a concentrated solution of benzamidine hydrochloride, is a thick oil which is decomposed into its constituents by hydrochloric acid, and into chloroform, &c., by aqueous alkalis. Under like conditions, benzamidine reacts with benzaldehyde, forming *benzylidenebenzamidine*, CHPh:N·CPh:NH; this is an oil which slowly crystallises in well-formed lustrous, long, transparent prisms, melts at 152°, is insoluble in water, very sparingly soluble in ether, readily soluble in hot alcohol, and when heated above its melting point is converted into cyanphenine.

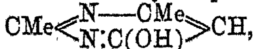
Benzamidine pyruvate, $C_7H_8N_2,C_3H_4O_3$, crystallises in lustrous scales, melts at 177°, is sparingly soluble in water, and is converted into benzamide when the solution is boiled; the *chloracetate*,

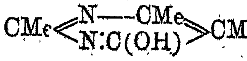
$$C_7H_8N_2,C_2H_3ClO_2,$$

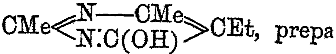
crystallises in white scales sparingly soluble in cold water; the *trichlorolactate*, $C_7H_8N_2,C_3H_3Cl_3O_3$, crystallises in small, white scales, is very sparingly soluble in cold water, and decomposes into benzamidine hydrochloride, carbonic anhydride, and dichloraldehyde when the aqueous solution is boiled.

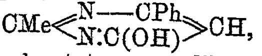
Benzoxamidine (benzenylamidoxime) combines with chloral hydrate forming a compound, $CPh(NOH)NH_2,C_2HCl_3O$, which crystallises in prisms melting at 132—133°. W. P. W.

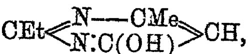
Pyrimidines (Metadiazines). By A. PINNER (*Ber.*, **22**, 1612—1635).—In former communications (compare Abstr., 1885, 158, 751; 1886, 45; 1887, 1053) the author has described the action of ethyl acetoacetate on amidines, and now gives in detail the results obtained by employing certain of its monosubstitution-derivatives. The method of preparation consists in mixing, in molecular proportion, the amidine hydrochloride, ethyl acetoacetate or one of its derivatives, and sodium hydroxide in 10 per cent. aqueous solution; an oil, probably an intermediate product, slowly separates and finally solidifies in the course of eight days or so. Pyrimidines are more readily obtained from aromatic than from fatty amidines, whilst on the other hand ethyl benzoylacetate, ethyl acetoxalate, and those substituted ethyl acetates which are more acid than ethyl acetoacetate, also seem to enter into reaction more readily than it. Experiments with ethyl diethacetoacetate and benzamidine hydrochloride seem to indicate that pyrimidines are not formed when disubstitution-derivatives of ethyl acetoacetate are employed, since benzamide was the sole product obtained, but in the author's opinion further experiments are needed before this conclusion can be definitely adopted.

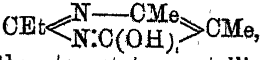
Dimethylhydroxypyrimidine,  $CMe<\begin{matrix}N—CMe\\N{:}C(OH)\end{matrix}>CH$, obtained from acetamidine and ethyl acetoacetate, crystallises in long needles, melts at 192°, is very soluble in the ordinary solvents, and, like all hydroxypyrimidines, form salts both with acids and bases. The *silver* salt, $C_6H_7N_2{\cdot}OAg$, is crystalline, dissolves readily in nitric acid or ammonia, and is fairly stable towards light. The hydroxypyrimidines can be alkylated in the presence of alcoholic potash in molecular proportion (comp. Wolner, Abstr., 1884, 1292), and when heated with the calculated quantity of alcoholic potash and an excess of ethyl bromide at 100° for some hours, dimethylhydroxypyrimidine yields the *hydrobromide* of *dimethylethoxypyrimidine*, $C_6H_7N_2{\cdot}OEt,HBr$. This crystallises in granular aggregates of prisms, decomposes without fusing when heated, is very soluble in water and in hot alcohol, and on treatment in aqueous solution with concentrated aqueous soda, is converted into *dimethylethoxypyrimidine*, which crystallises in long, white prisms, melts at 55° and boils at 258—260°.

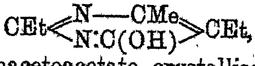
Trimethylhydroxypyrimidine,  $CMe<\begin{matrix}N—CMe\\N{:}C(OH)\end{matrix}>CMe$, formed from acetamidine and ethylic methacetoacetate, crystallises in aggregates of long, silky needles, melts at 168°, seems to distil without decomposition, and is very sparingly soluble in light petroleum, very soluble in water, though less so than the dimethyl-derivative, and readily soluble in hot alcohol, ether, and benzene.

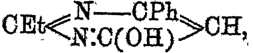
Dimethylethylhydroxypyrimidine,  $\mathrm{CMe}<\genfrac{}{}{0pt}{}{\mathrm{N—CMe}}{\mathrm{N{:}C(OH)}}>\mathrm{CEt}$, prepared from acetamidine and ethylic ethacetoacetate, crystallises in crusts of long needles, melts at 146°, and is readily soluble in water, alcohol, ether, and benzene, less soluble in light petroleum.

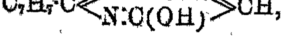
Methylphenylhydroxypyrimidine,  $\mathrm{CMe}<\genfrac{}{}{0pt}{}{\mathrm{N—CPh}}{\mathrm{N{:}C(OH)}}>\mathrm{CH}$, obtained from acetamidine and ethyl benzoylacetate, crystallises in long, slender needles, melts at 238°, is sparingly soluble in cold, readily soluble in hot alcohol, and dissolves readily in alkalis and in mineral acids.

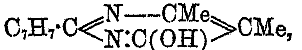
Ethylmethylhydroxypyrimidine,  $\mathrm{CEt}<\genfrac{}{}{0pt}{}{\mathrm{N—CMe}}{\mathrm{N{:}C(OH)}}>\mathrm{CH}$, formed from propionamidine and ethyl acetoacetate, crystallises in slender, white needles melting at 160°. On distillation at a low red heat with zinc-dust, it is reduced to *ethylmethylpyrimidine*, $C_4N_2H_2EtMe$, which boils at 160°, and in a moist vessel crystallises in long, white prisms owing probably to the formation of a hydrate. Experiments made with the object of obtaining oxidation products of ethylmethylpyrimidine were not successful, but when the solution obtained by dissolving the base in hydrochloric acid and adding platinic chloride and then dilute nitric acid is digested for some hours until the right concentration has been reached, gas is evolved and a yellow powder separates, which explodes when heated, and seems to be a *dichloronitroethylpyrimidine*, since the analytical numbers agree fairly well with those required for the formula $C_7H_7N_2Cl_2\cdot NO_2$.

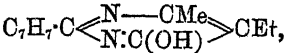
Ethyldimethylhydroxypyrimidine,  $\mathrm{CEt}<\genfrac{}{}{0pt}{}{\mathrm{N—CMe}}{\mathrm{N{:}C(OH)}}>\mathrm{CMe}$, prepared from propionamidine and ethylic methacetoacetate, crystallises in long, white, silky needles, melts at 165°, is readily soluble in water, alcohol, and ether, less so in benzene, and sparingly soluble in light petroleum. It is isomeric with Riess and v. Meyer's hydroxy-base of cyanmethethine (Abstr., 1885, 646).

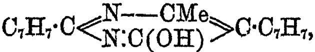
Diethylmethylhydroxypyrimidine,  $\mathrm{CEt}<\genfrac{}{}{0pt}{}{\mathrm{N—CMe}}{\mathrm{N{:}C(OH)}}>\mathrm{CEt}$, obtained from propionamidine and ethylic ethacetoacetate, crystallises in long, silky needles, melts at 135°, and is somewhat less soluble in water than its lower homologue. It is isomeric with v. Meyer's hydroxy-base of cyanethine (this vol., p. 577).

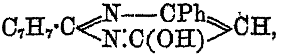
Ethylphenylhydroxypyrimidine,  $\mathrm{CEt}<\genfrac{}{}{0pt}{}{\mathrm{N—CPh}}{\mathrm{N{:}C(OH)}}>\mathrm{CH}$, formed from propionamidine and ethyl benzoylacetate, crystallises in long, thin, lustrous needles, melts at 238°, and is very slightly soluble in water, sparingly in hot alcohol.

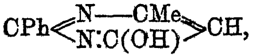
Benzylmethylhydroxypyrimidine,  $\mathrm{C_7H_7{\cdot}C}<\genfrac{}{}{0pt}{}{\mathrm{N—CMe}}{\mathrm{N{:}C(OH)}}>\mathrm{CH}$, prepared from phenylacetamidine and ethyl acetoacetate, crystallises in long prisms, melts at 175°, and is sparingly soluble in cold water, readily soluble in alcohol.

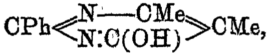
Benzyldimethylhydroxypyrimidine,  $\mathrm{C_7H_7{\cdot}C}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CMe}$, obtained from phenylacetamidine and ethylic methacetoacetate, is crystalline, melts at 181°, is more soluble in water than the preceding compound and readily soluble in alcohol and ether.

Benzylmethylethylhydroxypyrimidine,  $\mathrm{C_7H_7{\cdot}C}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CEt}$, formed from phenylacetamidine and ethylic ethacetoacetate, crystallises in long, thin, silky needles, melts at 193·5°, and in solubility resembles the preceding compound.

Dibenzylmethylhydroxypyrimidine,  $\mathrm{C_7H_7{\cdot}C}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{C{\cdot}C_7H_7}$, prepared from phenylacetamidine and ethylic benzylacetoacetate, crystallises in slender, matted needles, melts at 192°, and is insoluble in water, sparingly soluble in hot alcohol, and readily soluble in alkalis and acids.

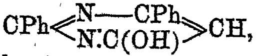
Benzylphenylhydroxypyrimidine,  $\mathrm{C_7H_7{\cdot}C}{<}\begin{matrix}\mathrm{N{-}CPh}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CH}$, obtained from phenylacetamidine and ethyl benzoylacetate, crystallises in granular aggregates of slender needles, melts at 233°, and is almost insoluble in water, but readily soluble in hot alcohol.

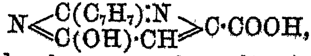
Phenylmethylhydroxypyrimidine,  $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CH}$, obtained from benzamidine and ethyl acetoacetate, has been previously described. It melts at 216°.

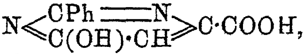
Phenyldimethylhydroxypyrimidine,  $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CMe}$, formed from benzamidine and ethylic methacetoacetate, crystallises in long, white needles, melts at 203°, and is sparingly soluble in hot water, very soluble in alcohol, acetic acid, alkalis, and mineral acids.

Phenylmethylethylhydroxypyrimidine, $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CEt}$, prepared from benzamidine and ethylic ethacetoacetate, crystallises in short, lustrous prisms, melts at 167°, and resembles the preceding compound in solubility.

Phenylmethylbenzylhydroxypyrimidine, $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}CMe}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{C{\cdot}C_7H_7}$, obtained from benzamidine and ethylic benzylacetoacetate, crystallises in silky needles, melts at 243°, and is insoluble in water and very sparingly soluble in alcohol.

Diphenylhydroxypyrimidine,  $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}CPh}\\\mathrm{N{:}C(OH)}\end{matrix}{>}\mathrm{CH}$, formed from benzamidine and ethyl benzoylacetate, crystallises in microscopic needles, melts at 284°, and is very sparingly soluble in hot alcohol, readily soluble in alkalis, mineral acids, and hot acetic acid.

Benzylhydroxypyrimidinecarboxylic acid,  $\mathrm{N}{<}\begin{matrix}\mathrm{C(C_7H_7){:}N}\\\mathrm{C(OH){\cdot}CH}\end{matrix}{>}\mathrm{C{\cdot}COOH}$, is prepared by mixing together, in molecular proportion, phenylacetamidine, ethyl acetoxalate, and aqueous soda, allowing the whole to remain for 14 days, adding more aqueous soda to dissolve the resinous mass which separates during the interval, and carefully treating the alkaline solution with hydrochloric acid. It crystallises in small prisms, melts at 230°, and is almost insoluble in water, readily soluble in alkalis and strong acids.

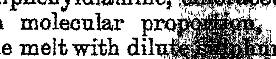
Phenylhydroxypyrimidinecarboxylic acid,  $N\!\lessgtr\!\begin{matrix}CPh{=\!=}N\\C(OH)\cdot CH\end{matrix}\!\!>\!C\cdot COOH$, is obtained by mixing benzamidine hydrochloride, ethyl acetoxalate, and aqueous soda in molecular proportion, and, after some days, filtering from the separated solid and precipitating the filtrate with hydrochloric acid. It crystallises in small, granular forms, melts at 247° with decomposition, is almost insoluble in water, readily soluble in hot alcohol and alkalis, but insoluble in dilute acids. The normal and basic *barium* salts and the *zinc* salt are described. When the crystalline solid filtered off in the preparation of the acid is extracted with acetone, the greater part is dissolved; the residue crystallised from water melts at 263°. The acetone solution contains *ethyloxalylacetylbenzamidine*, $NH\!:\!CPh\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, which crystallises in short, thick, lustrous prisms, melts at 180° with decomposition, and is sparingly soluble in water, readily soluble in alkalis, acetone, and alcohol. Alkalis convert it into the carboxylic acid, and when it is dissolved in ammonia and allowed to remain for some time it yields *phenylhydroxypyrimidinecarboxylamide*, $C_{10}H_7N_2O\cdot CONH_2$, which crystallises in short, thick, lustrous prisms, melts at a high temperature with decomposition, and is sparingly soluble in water.

Experiments are being made with a view to prepare pyrimidines by the condensation of amidines with ketonic acids and diketones. A mixture of ethyl oxalate, benzamidine hydrochloride and aqueous soda, in molecular proportion, yields *benzamidine ethyl oxalate*, $C_2O_4HEt,C_7H_8N_2$, which crystallises in slender, silky needles, melts at 197°, and is soluble in water and alcohol. A solution in dilute alcohol of benzil, benzamidine hydrochloride, and aqueous soda, in molecular proportion, when heated in a reflux apparatus for some hours, yields a compound, $C_{21}H_{16}N_2O$, which crystallises in highly refractive, hard, short prisms, melts at 232°, is sparingly soluble in cold alcohol, and seems to have the formula

$$NH\!:\!CPh\cdot N\!:\!CPh\cdot COPh,$$

since it is almost insoluble in water and alkalis. W. P. W.

Piperazines. By C. A. Bischoff (*Ber.*, **22**, 1774—1777).—An introduction to the following series of papers.

Ketopiperazines. By C. A. Bischoff and O. Nastvogel (*Ber.*, **22**, 1783—1786).—*Diphenylketopiperazine*,  $NPh\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CO\end{matrix}\!>\!NPh$, is formed by heating a mixture of ethylenediphenyldiamine, chloracetic acid and anhydrous sodium acetate, in molecular proportion, at 160—170°, and is purified by extracting the melt with dilute sulphuric acid and crystallising the residue from alcohol; the yield amounts to 53 per cent. of that theoretically possible. The addition of sodium acetate is necessary in order to obtain a pure product, since in its absence a higher temperature is required for the reaction, and an amorphous substance is obtained, which even after repeated purification melts as low as 120—130°. Diphenylketopiperazine melts at 148°, and is insoluble in water and light petroleum, but readily soluble in most other solvents. The sulphuric acid extract of the melt contains *acetylethylenediphenyldiamine*, $\mathrm{NPhAc{\cdot}CH_2{\cdot}CH_2{\cdot}NHPh}$, which can be precipitated by aqueous soda, and when crystallised from alcohol or hot water melts at 128°. A small quantity of diphenylpiperazine is also formed in the reaction.

When ethylenediphenyldiamine is heated with a molecular proportion of acetic anhydride at 120—130°, it yields acetanilide, diphenylpiperazine, acetylethylenediphenyldiamine, and *diacetylethylenediphenyldiamine*, $\mathrm{NPhAc{\cdot}CH_2{\cdot}CH_2{\cdot}NPhAc}$. The last-named compound is formed in larger quantity when twice the molecular proportion of acetic anhydride and a temperature of 140—150° are employed; it melts at 158°, and is readily soluble in alcohol, ether, chloroform, benzene, and acetic acid.

Diparatolylketopiperazine, $\mathrm{C_6H_4Me{\cdot}N}<\genfrac{}{}{0pt}{}{\mathrm{CH_2{\cdot}CH_2}}{\mathrm{CH_2{\cdot}CO}}>\mathrm{N{\cdot}C_6H_4Me}$, is obtained by heating ethylenediparatolyldiamine chloracetic acid and anhydrous sodium acetate in molecular proportion at 170°. It melts at 168·5°, is readily soluble in the ordinary solvents, except ether and water, and is not decomposed by boiling with aqueous potash.

W. P. W.

Hydrogenated Paradiazines of the Aromatic Series. By C. A. Bischoff (*Ber.*, 22, 1777—1783; compare Lellman and Schleich, this vol., p. 904).

—Diphenylpiperazine, $\mathrm{NPh}<\genfrac{}{}{0pt}{}{\mathrm{CH_2{\cdot}CH_2}}{\mathrm{CH_2{\cdot}CH_2}}>\mathrm{NPh}$ (Morley, Abstr., 1880, 112), or its homologues, can readily be prepared by heating a mixture of ethylene dibromide and aniline or its homologues, in molecular proportion, with enough sodium carbonate or acetate to take up the hydrogen bromide formed in the reaction. The temperature employed varies from 120° to 160°, according to the nature of the base, and in the case of aniline the yield of piperazine amounts to 80 per cent. of that theoretically possible. The melting point was found to be 163·5°, and determinations of the molecular weight by Raoult's method gave numbers agreeing well with that required by the generally accepted formula. The lower melting point found by Hofmann and Morley is not due to the presence of ethylenediphenyldiamine as impurity, but is caused by crystallisation with a small quantity of a basic substance melting at 122—123°. Diphenylpiperazine combines readily with diazosulphonic acids, forming azo-dyes; thus, with diazotised sulphanilic acid, a tetrazo-dye is obtained which is less soluble in water and dyes silk and wool a purer yellow than "helianthin," and with diazotised α-naphthylaminesulphonic acid a tetrazo-dye is formed which dyes silk and wool a fast bordeaux-red; these disazo-compounds do not dye unmordanted cotton. Morley's paradiamidodiphenylpiperazine, however, yields fast, direct cotton dyes when diazotised and combined with naphthylaminesulphonic and naphtholsulphonic acids; the compound obtained with β-naphthol-α-disulphonic acid (R-acid) gives a beautiful bluish-violet shade on cotton. The preparation of dyes belonging to other classes is being attempted, and it is mentioned that diphenylpiperazine yields with benzotrichloride a triphenylmethane-derivative, which forms salts resembling malachite-green in colour.

Diorthotolylpiperazine crystallises in colourless needles, but melts at 174° (comp. Mauthner and Suida, Abstr., 1886, 886).

Diparaditolylpiperazine, $C_{18}H_{22}N_2$, crystallises from benzene in colourless prisms, melts at 187—188°, and is very sparingly soluble in alcohol.

Di-α-naphthylpiperazine, $C_{24}H_{22}N_2$, crystallises from chloroform in colourless prisms, melts at 265°, and is very sparingly soluble in alcohol. The β-compound has not yet been obtained sufficiently pure for analysis.

Diparamethoxydiphenylpiperazine, $C_{16}H_{16}N_2(OMe)_2$, obtained from paranisidine and ethylene bromide, crystallises in well-formed tables, melts at 233°, and is very sparingly soluble in water, alcohol, and ether, but somewhat more soluble in hot benzene, chloroform, and acetone.

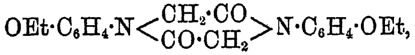
Diparaethoxydiphenylpiperazine, $C_{16}H_{16}N_2(OEt)_2$, prepared under like conditions from phenetidine, melts at 218°. W. P. W.

α-γ-Diketopiperazines. By C. A. Bischoff and O. Nastvogel (*Ber.*, **22**, 1786—1792).—Orthoditolyl-α-γ-diketopiperazine (Abenius and Widman, Abstr., 1888, 824), can be prepared by heating orthotolylglycine in a current of hydrogen at 150° so long as water is evolved, and then raising the temperature to 220°; very little carbonic anhydride is given off under these conditions. It melts at 159—160°, is insoluble in water, ether, and light petroleum, readily soluble in acetone, acetic acid, hot alcohol, and benzene, and by Raoult's method gives numbers agreeing with the generally accepted formula. The failure of Abenius and Widman to prepare this compound by heating orthotolylglycine (*J. pr. Chem.* [2], **38**, 303) is probably to be referred to the method of heating, since rapid heating would tend to favour the elimination of the elements of carbonic anhydride instead of water, with the consequent formation of secondary products. A study of the decomposition products of paraethoxyphenylglycine lends support to this view.

Paraethoxyphenylglycine, $OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot COOH$, obtained from phenetidine hydrochloride and chloracetic acid in the ordinary way, seems to crystallise with water, since the melting point rises from 120—125° to 163° by repeated crystallisation from hot water. The ammoniacal solution reduces silver nitrate, and the solution in dilute alcohol is coloured an intense bluish-violet by ferric chloride. When the glycine is rapidly heated at a high temperature, much more carbonic anhydride is evolved than when the heating is allowed to proceed more gradually, and when it is heated in a current of hydrogen at 260° until no further evolution of alcohol occurs, it yields paraethoxymethylaniline, diparaethoxyphenyl-α-γ-diketopiperazine, glycolyldiethoxyanilide, and an acid to which the formula $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot N(C_6H_4\cdot OEt)\cdot CH_2\cdot COOH$ is provisionally assigned from its analogy to the anilide of phenylimidodiacetic acid (compare Hausdörfer, p. 1013); no trace of a carbamide-derivative could, however, be detected (compare Abenius and Widman, *loc. cit.*).

Paraethoxymethylaniline, $OEt\cdot C_6H_4\cdot NHMe$, boils at 251°, becomes rapidly coloured even in a closed vessel, and yields a crystalline hydrochloride.

Paradiethoxydiphenyl-α-γ-diketopiperazine,



$$OEt\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CO\\ CO\cdot CH_2\end{matrix}>N\cdot C_6H_4\cdot OEt,$$

crystallises in slender needles, melts at 265°, and is very sparingly soluble in the ordinary solvents.

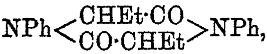
Glycolyldiethoxyanilide, $OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, crystallises from benzene in lustrous, well-formed tables, melts at 139—140°, and is sparingly soluble in hydrochloric acid. It may also be obtained by the action of phenetidine on glycine.

The acid, provisionally regarded as the *ethoxyanilide* of *paraethoxyphenylimidodiacetic acid*, melts at 157°, is insoluble in water, and yields no colour on treatment with ferric chloride. The fact that it does not undergo condensation into a piazine-derivative at a temperature of 260—300°, seems to support the view of its constitution taken by the authors. W. P. W.

Homologues of Diphenyl-α-γ-diketopiperazine. By O. NASTVOGEL (*Ber.*, **22**, 1792—1795).—*Ethyl α-anilidopropionate*,

$$NHPh\cdot CHMe\cdot COOEt,$$

is formed almost quantitatively on heating aniline with ethyl α-bromopropionate at 100°, boils without decomposition at 272° under a pressure of 757 mm., and has a sp. gr. = 1·060 at 19·5° compared with water at the same temperature. When saponified with aqueous potash, it is converted into Tiemann's α-anilidopropionic acid (Abstr., 1883, 199), and this, when heated with an excess of aniline in a reflux apparatus, yields the corresponding *anilide*, $NHPh\cdot CHMe\cdot CONHPh$, which crystallises from alcohol in long, colourless needles, melts at 126°, and is readily soluble in water and the ordinary solvents. Direct heating of α-anilidopropionic acid results in the formation of a small quantity of *diphenyl-α-γ-dimethyl-β-δ-diketopiperazine*, $NPh<\begin{matrix}CHMe\cdot CO\\ CO\cdot CHMe\end{matrix}>NPh$, melting at 180—181°. The large quantity of accompanying products, including ethylaniline, render it difficult to purify the compound, and a far better yield is obtained by heating the acid at a lower temperature with the calculated quantity of acetic anhydride. Under these conditions, only a very small quantity of carbonic anhydride is evolved, and two piperazines are obtained, one of which is identical with that just described, and the second melts at 147—148°. Both are insoluble in water and hydrochloric acid, and are about equally soluble in most indifferent solvents except ether, in which the compound of lower melting point is the more soluble. Towards alkalis they behave like ketopiperazines, but further experiments are required before it can be decided whether the two compounds are geometrical isomerides or not.

Ethyl α-anilidobutyrate, $NHPh·CHEt·COOEt$, obtained under like conditions from aniline and ethyl α-bromobutyrate, boils at 278° under a pressure of 754 mm., and has a sp. gr. = 1·045 at 19°. On saponification, it yields α-anilidobutyric acid (Duvillier, Abstr., 1881, 87) melting at 139—140°, and when this acid is heated with acetic anhydride it is converted into *diphenyl-α-γ-diethyl-β-δ-diketopiperazine*,  $NPh<\begin{matrix}CHEt·CO\\CO·CHEt\end{matrix}>NPh$, which crystallises in slender, silky needles, melts at 260°, and is sparingly soluble in alcohol.

W. P. W.

Diphenyl-α-γ- and α-δ-Diketopiperazine. By A. Hausdörfer (*Ber.*, **22**, 1795—1804).—The author has repeated the experiments of Rebuffat (Abstr., 1887, 1108) and Abenius (Abstr., 1888, 854) on the aromatic acetamido-compounds. When aniline (2 mols.) and chloracetic acid (1 mol.) are heated together for about three hours at the temperature of a salt-water bath, a melt is obtained from which water extracts phenylglycine and phenylimidodiacetic acid (see further), both being present in small quantity. The yellow, resinous mass, insoluble in water, contains Rebuffat's supposed phenylglycine-phenylamidoacetic acid, which can be extracted by digestion with ammonia, and also phenylglycinanilide, and Meyer's (Abstr., 1878, 294) and Abenius' diphenyl-α-γ-diketopiperazine. If the conditions are modified so that aniline and chloracetic acid in molecular proportion are heated with an equal weight of anhydrous sodium acetate for half an hour at 110—120°, and then for 3—4 hours at 140—150°, a resinous mass is formed, from which acetylphenylglycine, Rebuffat's acid, phenylglycinanilide and diphenyl-α-γ-diketopiperazine can be isolated. Rebuffat's acid is also obtained as the chief product on heating phenylglycinanilide and chloracetic acid, in molecular proportion, either alone or with anhydrous sodium acetate, at 140—150°. In all these cases, Rebuffat's acid is found to crystallise in colourless, silky needles melting at 211—213°, instead of scales melting at 190—195°, and its formation from phenylglycinanilide and chloracetic acid indicates that it must be regarded as the anilide of phenylimidodiacetic acid.

Phenylglycine is best prepared by heating aniline (25 grams), chloracetic acid (25 grams), and hydrated sodium acetate (40 grams) on a water-bath for 30—40 minutes, a few c.c. of water being added when the mixture has become fused; the yield amounts to 10—12 grams, and at the same time 3—4 grams of phenylimidodiacetic acid are also formed.

Phenylimidodiacetic acid, $NPh(CH_2·COOH)_2$, is readily obtained by heating a mixture of phenylglycine, chloracetic acid, and anhydrous sodium acetate in molecular proportion for some time at 120—130°; the melt is extracted with ammonium carbonate solution, the filtrate acidified with hydrochloric acid, and the acid separated, by extraction with ether, from the methylaniline formed simultaneously by the partial decomposition of the phenylglycine. It crystallises in colourless, silky needles, melts at 150—155° with partial decomposition, is readily soluble in alcohol and hot water, and decomposes with evolution of carbonic anhydride when its aqueous solution is boiled. The *anilide*, $CO(NHPh)\cdot CH_2\cdot NPh\cdot CH_2\cdot COOH$, is formed by gradually heating aniline with the acid in molecular proportion at 180°; it crystallises from dilute alcohol in silky needles, melts at 211—213° with decomposition, and is identical with Rebuffat's acid. The *dianilide*, $NPh(CH_2\cdot CONHPh)_2$, is also obtained under these conditions, and in larger quantity when twice the molecular proportion of aniline is employed; it crystallises in colourless needles, melts at 218°, and is very sparingly soluble in alcohol. Aniline hydrogen phenylimidodiacetate crystallises from water in needles, decomposes at 150—151°, not at 99° as stated by Meyer (Abstr., 1882, 519), and when heated at 150—160° for some time is converted into the anilide melting at 211—213°; the normal salt could not be obtained.

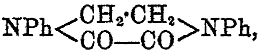
When a mixture of phenylglycinanilide, ethyl chloracetate, and anhydrous sodium acetate in molecular proportion are heated either alone or in alcoholic solution at 140—150° for 3—4 hours, the *anilide of ethyl hydrogen phenylimidodiacetate*, $CO(NHPh)\cdot CH_2\cdot NPh\cdot CH_2\cdot COOEt$, is obtained. It crystallises in granular aggregates of small needles, melts at 121—122°, is readily soluble in alcohol and ether, and is saponified by aqueous or alcoholic potash, and even by an aqueous solution of sodium carbonate. Diphenyl-α-γ-diketopiperazine is also formed in small quantity in this reaction, and can further be obtained by warming a mixture of phenylglycinanilide with the calculated quantity of sodium ethoxide, and adding ethyl chloracetate in molecular proportion.

Diphenyl-α-δ-diketopiperazine, $NPh<\begin{matrix}CO\cdot CH_2\\ CO\cdot CH_2\end{matrix}>NPh$, is obtained when the anilide of phenylimidodiacetic acid is heated with acetic anhydride in a reflux apparatus at 140° for some time, and finally at 180—190°. It crystallises in colourless, silky needles, melts at 152—153°, and is soluble in ether and alcohol.

Diphenyl-α-γ-diketopiperazine decomposes into phenylglycine when heated in a reflux apparatus with a large excess of 10 per cent. alcoholic potash, but yields phenylglycinylphenylglycine (Abenius, *loc. cit.*) when treated in molecular proportion with potassium hydroxide in alcoholic solution, and either allowed to remain in the cold for some time, or heated in a reflux apparatus. Phenylglycinylphenylglycine is also formed, together with diphenyl-α-γ-diketopiperazine, by heating a mixture of bromacetylphenylglycine, aniline, and hydrated sodium acetate in molecular proportion for a short time at 100°, and this reaction serves to show that Abenius' formula is correct. The formation of the piperazine is readily explained, since the glycine is converted into diphenyl-α-γ-diketopiperazine either by heating it at its melting point (129°) or by allowing its solution in dilute hydrochloric acid to remain in the cold for some time.

W. P. W.

α-β-Diketopiperazines. By C. A. Bischoff and O. Nastvogel (*Ber.*, **22**, 1804—1808).—*Diphenyl-α-β-diketopiperazine*,

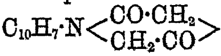


$$NPh<{CH_2\cdot CH_2 \atop CO—CO}>NPh,$$

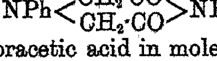
is formed by heating ethylenediphenyldiamine and oxalic acid at 200° for some time, and crystallises in colourless, lustrous scales, melts at 258°, and is very sparingly soluble in alcohol, ether, benzene, light petroleum, and carbon bisulphide, though somewhat more soluble in chloroform and acetic acid.

Diorthotolyl-α-β-diketopiperazine, obtained under like conditions from ethylenediorthotolyldiamine, melts at 183·5—184°, and is soluble in chloroform and acetic acid.

The reactions of oxalic acid with secondary diamines, however, do not always proceed normally; thus paratolylglycinetoluidide when heated with the acid does not form a triketopiperazine, but yields Abenius' diparatolyldiketopiperazine (Abstr., 1888, 854). Abnormal results are also obtained in other cases; thus ethyl malonate and ethylenediphenyldiamine react with the formation of diphenylpiperazine, whilst phenylglycinanilide is decomposed by succinic acid with the production of succinanil.

With α-naphthylamine in the cold, chloracetic acid forms an additive compound, $C_{10}H_7\cdot NH_2,CH_2Cl\cdot COOH$, which melts at 90°, is readily soluble in the ordinary solvents, and is decomposed by aqueous soda into its components; when the two compounds are heated, however, a dinaphthyl-α-γ-diketopiperazine,  $C_{10}H_7\cdot N<{CO\cdot CH_2 \atop CH_2\cdot CO}>N\cdot C_{10}H_7$, seems to be formed.

α-Naphthylglycine, $C_{10}H_7\cdot NH\cdot CH_2\cdot COOH$, is obtained by heating α-naphthylamine, chloracetic acid, and sodium acetate at 100°; it melts at 198—199°, and is insoluble in benzene, ether, and light petroleum, sparingly soluble in alcohol, and readily soluble in acetone and acetic acid. When heated in a current of carbonic anhydride at 230°, it is converted into the *anhydride*, $(C_{10}H_7\cdot NH\cdot CH_2\cdot CO)_2O$, which crystallises in small, lustrous scales, melts at 268—269°, and is insoluble in acids, alkalis, ether, and light petroleum, but soluble in hot benzene, alcohol, acetic acid, and chloroform. W. P. W.

Characteristics of the Piperazines. By C. A. Bischoff (*Ber.*, **22**, 1809—1812).—*Phenyl-α-δ-diketopiperazine*,  $NPh<{CH_2\cdot CO \atop CH_2\cdot CO}>NH$, is obtained when a mixture of aniline and chloracetic acid in molecular proportion is carefully heated, and crystallises from dilute alcohol in colourless prisms melting at 158°. If sodium acetate is present and the mixture is heated at 120—130°, the reaction takes a different course with the formation of phenylglycocollamide. The remainder of the paper is devoted to a recapitulation of the various reactions in which piperazines are formed. W. P. W.

Methylpyrrolidine. By J. Tafel and A. Neugebauer (*Ber.*, **22**, 1865—1867; compare Abstr., 1886, 463).—2-Methylpyrrolidine is best prepared by adding a boiling amyl alcoholic solution of methylpyrrolidone (compare p. 961) to a large excess of sodium and warming on the water-bath with constant shaking until the reaction is at an end; the formation of sodium γ-amidovalerate is in this way to some extent avoided and the yield is increased by about one half. This base, like the isomeric compound described by Oldbach (Abstr., 1887, 735), is not identical with the base obtained by Brieger (*ibid.*, 285) from the tetanus bacillus. The *hydrochloride*, C_5NH_{11},HCl, crystallises in colourless prisms melting at about 210—220°. The *oxalate*, $(C_5NH_{11})_2,C_2H_2O_4$, crystallises in small needles melting at 165—168°. The *platinochloride*, $(C_5NH_{11})_2,H_2PtCl_6 + H_2O$, crystallises from hot water in long, golden needles, does not lose its water at 100°, and is very sparingly soluble in hot alcohol but very readily in water. The *aurochloride*, C_5NH_{11},H_2AuCl_5, forms golden, rhombic crystals, melts at 140—144°, and is readily soluble in water and alcohol. The *nitroso-derivative*, prepared by treating a concentrated aqueous solution of the base with sodium nitrite and dilute sulphuric acid, is a yellow oil; it gives Liebermann's reaction, and is readily reduced by glacial acetic acid and zinc-dust, yielding a base, probably the corresponding hydrazine, which is soluble in ether.

Dimethylpyrrolidine methiodide, $C_6H_{13}N,MeI$, is obtained, together with dimethylpyrrolidine hydriodide, when methylpyrrolidine is boiled with excess of methyl iodide in methyl alcoholic solution. It separates from hot alcohol in colourless, spear-shaped crystals, and is readily soluble in water. *Dimethypyrrolidone* is an oil boiling at about 102°.

F. S. K.

Pyridineorthodicarboxylic Acid. By G. GOLDSCHMIEDT and H. STRACHE (*Monatsh.*, **10**, 156—160).—Cinchomeronic acid, like quinolinic acid (compare Bernthsen and Mettegang, Abstr., 1887, 737), is converted into its anhydride, $C_5H_3N(CO)_2O$, when boiled with acetic anhydride. The product crystallises from chloroform in plates which melt at 76—77°, and may be sublimed unchanged. On treatment with absolute alcohol it gives the ethyl salt,

$$COOH{\cdot}C_5H_3N{\cdot}COOEt,$$

which crystallises from benzene in plates melting at 131—133°, and which with silver nitrate gives the salt $C_7H_3NO_4AgEt$, crystallising in long needles. The methyl salt, $COOH{\cdot}C_5H_3N{\cdot}COOMe$, melts at 152—154°, and much resembles the ethyl salt in general properties. When gaseous ammonia is passed through a solution of the anhydride in benzene, ammonium amidocinchomeronate, $CONH_2{\cdot}C_5H_3N{\cdot}COONH_4$, a microcrystalline, hygroscopic powder, melting at 228—229°, is formed. The silver salt forms microscopic needles; the free acid crystallises in needles which melt with decomposition at 237°. On heating the ammonium salt in an air-bath at 120°, it decomposes, forming imidocinchomeronic acid, a yellow powder which melts at 229—230° and readily sublimes.

Papaveronic acid, which is cinchomeronic acid in which an atom of hydrogen is displaced by the group $CH_2{\cdot}C_6H_3(OMe)_2$ (compare Goldschmiedt, Abstr., 1888, 1118), when heated with acetic anhydride, yields an anhydride which crystallises from benzene in spherical groups of needles melting at 169—170°, from which, by boiling with alcohol, the monethyl salt, crystallising in small needles, melting at 187—188°, is obtained. Dry ammonia acts on the anhydride with formation of an acid amide. G. T. M.

Myristic Aldehyde. By F. KRAFFT and I. MAI (*Ber.*, **22**, 1757—1759).—*Ethyl hydrotridecyllutidinedicarboxylate*,

$$C_{20}H_{35}N(COOEt)_2,$$

is obtained when a mixture of myristic aldehyde (20 grams), alcoholic ammonia (40 c.c.), and ethyl acetoacetate (26 grams) is heated for eight to nine hours in a reflux apparatus; it crystallises from alcohol in hard, glassy forms, and melts at 60°. On treatment in alcoholic solution with nitrous acid, it is converted into the *hydrochloride* of *ethyl tridecyllutidinedicarboxylate*, $C_{20}H_{33}N(COOEt)_2,HCl$, which crystallises in silky needles. The *ethyl*-salt, obtained by the action of aqueous soda on the hydrochloride, is an oil and distils without decomposition at 265°. When saponified with alcoholic potash, this compound is converted into the *hydrochloride* of *tridecyllutidinedicarboxylic acid*, $C_{20}H_{33}N(COOEt)_2,HCl$, which is crystalline, and yields *tridecyllutidine*, $C_{20}H_{35}N$, on distillation with soda-lime. This base boils at 215—217° under a pressure of 13 mm., has a slight pyridine-like odour, and forms a *platinochloride*, $(C_{20}H_{35}N)_2,H_2PtCl_6$, crystallising in small, yellow scales. W. P. W.

Ethyl Cinchonate and Cinchonamide. By A. P. VAN DER KOLF and F. H. VAN LEENT (*Rec. Trav. Chim.*, **8**, 217—221).—*Ethyl cinchonate*, $C_9NH_6{\cdot}COOEt$, was obtained by saturating with hydrogen chloride absolute alcohol holding cinchonic acid in suspension, and warming until the cinchoninic acid dissolved. A current of air was then passed through the solution to expel some of the hydrogen chloride; sodium carbonate was added, and the ethyl cinchonate extracted with benzene. It could not be distilled, for even at 15 mm. pressure it decomposes at 110°, giving off quinoline. It was purified by repeated crystallisation from ether, and then formed colourless crystals melting at 13°. Compounds with mercuric chloride and with platinum chloride were prepared; these melt at 153° and 204° respectively, and were found to have the formulæ $C_{12}H_{11}NO_2,HgCl_2$ and $(C_{12}H_{11}NO_2)_2,H_2PtCl_6$.

When ethyl cinchonate is heated at 100° with saturated aqueous ammonia in a sealed tube it dissolves, and white crystals of *cinchonamide*, $C_9NH_6{\cdot}CONH_2$, melting at 181°, are deposited. The platinochloride, $(C_{10}H_8N_2O)_2,H_2PtCl_6$, forms orange-red tables melting at 250—255°. C. F. B.

Caffeïne. By R. LEIPEN (*Monatsh.*, **10**, 184—188).—When oxygen, previously ozonised in the Siemen's ozoniser, is passed through water in which caffeïne is suspended until the solution obtained is perfectly clear (2—3 grams of caffeïne were dissolved in about 24 hours), the same products, namely, dimethylparabanic acid, ammonia, methylamine, and carbonic anhydride are obtained as when caffeïne is oxidised with chromic mixture (compare Maly and Hinteregger, Abstr., 1881, 747).

Caffeïne oxalate may be prepared by direct addition of oxalic acid to caffeïne. It forms colourless needles, and unlike other caffeïne salts (compare Schmiedt, Abstr., 1881, 746) is perfectly stable in presence of water, from which it may be readily recrystallised.

G. T. M.

Morphine. By Z. H. Skraup and L. Wiegmann (*Monatsh.*, **10**, 110—114; compare Abstr., 1882, 218 and 1112; 1884, 613; and 1886, 562).—When morphine is heated at a high temperature with alcoholic potash, a phenol-like compound and a volatile amine are formed. The best yield (40 per cent.) of the latter is obtained when morphine is mixed with 10 to 15 times its weight of a 20 per cent. solution of alcoholic potash, and heated at 180° for 4 to 6 hours, air being carefully excluded during the process. On adding the contents of the tube in which the operation was conducted to dilute sulphuric acid, a light brown flocculent substance, which is probably a dihydroxymorphine, $C_{17}H_{19}NO_5$, separates; this is purified by dissolving it in a dilute alcoholic solution of sodium hydrogen sulphite, and fractional precipitation with water, when it is obtained in microcrystalline flocks. It is exceedingly unstable, all attempts to investigate it yielding unsatisfactory results. The volatile amine, *ethylmethylamine*, boils at 34—35°, its hydrochloride melting at 133°, its platinochloride at 208°, and its aurochloride at 179—180°. The amine was also prepared synthetically by the action of methyl iodide on a mixture of ethylamine and ethyl alcohol, &c.

Fischer, Schrötter, and v. Gerichten have shown that morphine is a derivative of phenanthrene, but the conclusions derived from the study of the alkyl-derivatives by different investigators are of a contradictory nature. From the results obtained by the authors, it appears that the nitrogen-atom in morphine is directly combined with two alkyl-groups, a conclusion in direct opposition to that arrived at by Knorr (this vol., p. 417). The authors also obtained methylethylamine from morphine when alcohol previously distilled over oxalic acid was used, and from morphine and codeïne by heating them with methyl alcoholic potash. There is consequently no doubt that morphine contains both an ethyl- and a methyl-group directly united to the nitrogen-atom. That the methylethylamine does not result from the decomposition of previously formed propylamine appears certain, as that compound is not changed when it is heated with alcoholic potash under the same conditions as those described above in the case of morphine.

G. T. M.

Ecgonine and Anhydroecgonine. By A. Einhorn (*Ber.*, **22**, 1495).—In aqueous solution, ecgonine hydrochloride has the specific rotatory power $[\alpha]_D = 57°$, and anhydroecgonine hydrochloride the specific rotatory power $[\alpha]_D = 61·5°$.

F. S. K.

Cupreïne. By A. C. Oudemans, Jun. (*Rec. Trav. Chim.*, **8**, 147—172; comp. Hesse, Abstr., 1886, 83, and Paul and Cownley, *ibid.*, 1885, 563).—The pure base was prepared as follows:—The commercial basic sulphate was converted into the neutral hydrochloride by heating it with 10 times its weight of water, and adding hydrochloric acid until a clear solution was obtained. To this was added the calculated quantity of barium chloride required to precipitate the sulphuric acid, the solution being continually shaken; the precipitate was allowed to settle, the liquid filtered through animal charcoal, and, when cold, poured little by little into a dilute solution of ammonia, which was shaken continually; finally, the precipitate thus obtained was washed rapidly with cold water. If any had become coloured, it was digested with 70 per cent. alcohol, and the residue dissolved in alcohol, and precipitated by the cautious addition of water; the alkaloïd was thus obtained perfectly white and pure. Its formula is $3(C_{19}H_{22}N_2O_2) + H_2O$. When anhydrous, it melts at 197°; its specific rotatory power is $[\alpha]_D = 175·4°$ in dilute aqueous or alcoholic solution.

Various salts were prepared, and their solubility in water and their specific rotatory power determined. The solubility was determined at temperatures varying between 15° and 17°, and is given below in terms of the anhydrous salt. The specific rotatory power was determined at 17° for aqueous (and in some cases also for alcoholic) solutions of varying concentration; it was found that its value increased with the dilution of the solutions, and was generally somewhat higher for alcoholic than for aqueous solutions of the same strength. The values given below are those obtained with the most

Formula.	100 parts of water dissolve	Specific rotatory power		
		concentration $= \frac{p}{V}$.	of the salt.	of the base.
$3(C_{19}H_{22}N_2O_2),H_2O$..............	—	0·0069	—	−175·4°
$C_{19}H_{22}N_2O_2,HCl + H_2O$.........	1·78	0·0056	−157·1°	−184·7
$C_{19}H_{22}N_2O_2,2HCl$ ...... ,, ,, $+ H_2O$......	17·1	0·0109 0·0119	−211·0	−283·8
$C_{19}H_{22}N_2O_2,HBr + H_2O$.........	0·82	0·0049	−145·8	−192·7
$C_{19}H_{22}N_2O_2,2HBr$ .... ,, ,, $+ 2H_2O$	7·99	0·0156	−189·0	−287·7
$C_{19}H_{22}N_2O_2,HI$	0·94	0·0080	−126·3	−178·4
$C_{19}H_{22}N_2O_2,2HI + H_2O$....... ,, ,, $+ 2H_2O$......	6·67	0·0150	−151·2	−283·2
$C_{19}H_{22}N_2O_2,HNO_3 + 2H_2O$......	1·06	0·0113	−138·4	−182·5
$C_{19}H_{22}N_2O_2,2HNO_3 + H_2O$......	8·20	0·0128	−179·4	−289·1
$C_{19}H_{22}N_2O_2,HClO_3$..............	2·08	0·0103	−144·9	−184·4
$2(C_{19}H_{22}N_2O_2),H_2SO_4 + 6H_2O$....	0·12	—	—	—
	0·48 (at 100°)	—	—	—
$C_{19}H_{22}N_2O_2,H_2SO_4 + 2H_2O$......	1·36	0·0095	−202·4	−289·9
$C_{19}H_{22}N_2O_2,CH_2O_2$.............	0·91	0·0048	−163·8	−183·0
$C_{19}H_{22}N_2O_2,C_2H_4O_2 + 2H_2O$......	1·18	—	—	—
	5·88 (at 100°)	—	—	—
$2(C_{19}H_{22}N_2O_2),C_2H_2O_4 + 2H_2O$ ..	0·25	—	—	—
$2(C_{19}H_{22}N_2O_2),C_4H_6O_6 + 2H_2O$ ..	0·17	—	—	—

dilute solutions used. They are calculated from the formula $[\alpha]_D = V\alpha/lp$. In the case of cupreïne dihydrochloride, the specific rotatory power was found to diminish with the addition of free hydrochloric acid to the solution.

It was also found that the calculated specific rotatory power of the base is much greater in the normal than in the basic salts. It has nearly constant values of 285·4° and 185·4° respectively. The salts, with 2 mols. of a monobasic acid, are also more soluble than those with 1 mol.

The table (p. 1019) summarises the data regarding the salts of cupreïne; many of these salts have already been prepared by Hesse, or by Paul and Cownley.

The following salts were also prepared, but as they were not well characterised, nothing but an analysis of them was attempted, and not even this in all cases :—

$C_{19}H_{22}N_2O_2,2HClO_3 + XH_2O$; $C_{19}H_{22}N_2O_2,HClO_4 + 1\frac{1}{2}H_2O$;
$C_{19}H_{22}N_2O_2,2HClO_4 + 2H_2O$; $C_{19}H_{22}N_2O_2,2H_2SO_4 + 3H_2O$;
$C_{19}H_{22}N_2O_2,2CH_2O_2 + XH_2O$; $C_{19}H_{22}N_2O_2,2C_2H_4O_2 + XH_2O$;
$C_{19}H_{22}N_2O_2,2C_2H_2O_4 + XH_2O$; $C_{19}H_{22}N_2O_2,C_4H_6O_6 + XH_2O$;
$C_{19}H_{22}N_2O_2,2C_4H_6O_6 + H_2O$; $C_{19}H_{22}N_2O_2,H_2PtCl_6 + H_2O$.

C. F. B.

Pseudephedrine. By A. LADENBURG and C. OELSCHLÄGEL (*Ber.*, **22**, 1823—1827).—Nagai, some years ago, isolated an alkaloïd, ephedrine, from the *Ephedra vulgaris*, but through lack of material was unable to do more than determine its physiological action, and ascertain the melting point (210°) of its hydrochloride. Recently, a second compound has been obtained by Merck from plants belonging to the same genus. This substance, provisionally termed pseudephedrine, is isolated by extracting the roots with alcohol, distilling off the alcohol from the filtrate, treating the residue with ammonia, extracting with chloroform, and, after evaporation of the chloroform, converting the crude base into hydrochloride, which is further purified by repeated crystallisation from ether-alcohol.

Pseudephedrine, $C_{10}H_{15}NO$, obtained from the hydrochloride by precipitation with potassium carbonate, crystallises from ether in beautiful, measurable forms, melts at 114—115°, has a faint, pleasant odour, and is readily soluble in ether and alcohol, sparingly soluble in cold water. As determined by Raoult's method with phenol as solvent, the molecular weight is found to be about 175. The *hydrochloride*, $C_{10}H_{15}NO,HCl$, crystallises in colourless, slender needles, melts at 176°, and is very soluble in water and alcohol; the *hydrobromide*, $C_{10}H_{15}NO,HBr$, melts at 174—175°; the *hydriodide*, $C_{10}H_{15}NO,HI$, melts at 165°; the *aurochloride*, $C_{10}H_{15}NO,HAuCl_4$, crystallises from water in long, branching needles; the *picrate*, *cadmioiodide*, *bismuthoiodide*, and *platinochloride* are oily substances. The *nitrosamine*, $C_{10}H_{14}N_2O_2$, melts at 80—82°; and the *dibenzoyl*-derivative, $C_{10}H_{13}NOBz_2$, melts at 119—120°. On oxidation with potassium permanganate, pseudephedrine yields benzoic acid. When heated with concentrated hydrochloric acid at 180° for 3—4 hours, it gives an oil which decomposes for the most part on distillation in a vacuum; a small portion, however, distils over at 130—150°, and yields methylamine and benzoic acid on oxidation with potassium permanganate. The authors provisionally assign the formula CHPh(OH)·CHMe·NHMe, to pseudephredine. The alkaloïd is poisonous, and when taken internally produces mydriasis, although a 1 per cent. solution applied to the eye does not cause any dilatation of the pupil. W. P. W.

Nucleïn. By L. LIEBERMAN (*Chem. Centr.*, 1889, 540—541, and 590, from *Centr. med. Wiss.*, 1889, 210—212, and 225—227).—The author now shows that the presence of metaphosphoric acid in nucleïn may be proved without preparing the pure substance. If the yolk of hen's egg is treated with dilute hydrochloric acid, and the filtrate added to a clear solution of white of egg, a much heavier precipitate occurs than is produced by the action of hydrochloric acid alone. This precipitate shows all the properties of nucleïn.

If an alkaline solution of xanthine is added to a clear solution of white of egg also alkaline, a precipitate is obtained by adding the metaphosphoric acid in excess. After washing with cold water, and treatment with ammonia or boiling water, xanthine may be detected in either solution. Nucleïn obtained from yeast behaves exactly like this.

Guanine, dissolved in dilute sodium hydroxide, produces first a white, flocculent precipitate on the addition of metaphosphoric acid, which becomes crystalline on adding an excess of the precipitate. The flocculent precipitate contains guanine, metaphosphoric acid, and soda, whilst the crystalline precipitate consists of pure guanine. Xanthine and guanine appear, therefore, to be merely mixed with the nucleïn. Hypoxanthine, on the other hand, seems to be combined with some other substance, such as adenine or carnine, which accompany nucleïn. J. W. L.

Decomposition Products of Caseïn. By E. DRECHSEL (*J. pr. Chem.* [2], **39**, 425—429).—By treating caseïn with concentrated hydrochloric acid and stannous chloride, Hlasiwetz and Habermann obtained leucine, tyrosine, glutamic acid, aspartic acid, ammonia, and a thick, uncrystallisable liquid; the author treated this liquid with phosphotungstic acid, and obtained a precipitate which was washed with 5 per cent. sulphuric acid, and heated with baryta-water; the filtrate, after precipitating the excess of barium, was evaporated with hydrochloric acid. The *hydrochloride*, $C_7H_{14}N_2O_2Cl_2$, of a strong base was thus obtained; its *platinochloride*, $C_7H_{14}N_2O_2PtCl_6 + 4H_2O$, forms long, reddish-yellow prisms.

When alcoholic platinic chloride was added to the mother-liquor from the above hydrochloride, the *platinochloride*, $C_8H_{16}N_2O_2Cl_2PtCl_4 + H_2O$, of another base, homologous with the above, was obtained.

The author considers that these bases form an important departure in the investigation of the albuminoïds. A. G. B.

Physiological Chemistry.

Influence of "Saccharin" on Digestion. By STIFT (*Bied. Centr.*, **18**, 458—460).—"Saccharin" is not capable of being digested, but passes unchanged through the organism. In experiments made by the author with himself, in which 3 grams of "saccharin" a day was taken, a slight purgative action was observed and afterwards a loss of appetite. To ascertain the action, if any, of "saccharin" on digestive ferments, experiments were made with meat, egg-albumin, caseïn, and pea-meal, with and without, the addition of "saccharin." The presence of "saccharin" delayed the solution of the albuminoïds, which was not complete after 12 hours' contact with the gastric juice. The greater the amount of "saccharin" present, the more marked was its action. Similar results were obtained with the pancreatic ferment and with diastase. As the whole process of digestion is a series of ferment-actions, "saccharin" must be considered as a substance which interferes with digestion, and therefore injurious to health. N. H. M.

Food of Larval Bees. By A. v. PLANTA (*Zeit. physiol., Chem.*, **13**, 552—561).—In a former communication (Abstr., 1888, 733), it was stated that the food of the larval drones was different during the first four days and the last four days of larval existence. The same is now found to be the case with the working bees. It was necessary to empty as many as 4000 cells in order to obtain sufficient material to work with. The queen bees have the same food throughout.

The composition of the food material is shown in the following table:—

	Queen.	Drones.		Working-bees.	
		Under 4 days.	Over 4 days.	Under 4 days.	Over 4 days.
Nitrogenous material..	45·14	55·91	31·67	53·38	27·87
Fat	13·55	11·90	4·74	8·38	3·69
Glucose	20·39	9·57	38·49	18·09	44·93

The above numbers are percentages of dry material.

The queen larvæ receive during the whole of their larval condition (seven days) a food which is already digested, and which is especially rich in proteïds.

The drone larvæ receive, until the fourth day, a fully digested food which is even richer in proteïd than the queen's food; no doubt this is to hurry on development. After the fourth day, when the larvæ are strong, the feeding bees are not so painstaking, they prepare only a small part of the food by digesting it, and add to it raw materials in the form of pollen grains and honey. Among the factors in causing this change of diet, must be want of time; for during the months of May and June the bees have to feed daily 15,000—20,000 larvæ.

With regard to the working bees, much the same may be said, except that pollen grains are never added to the food after the fourth day, but the change in diet is produced simply by admixture with honey. This is probably because the cells of the larval workers are so small; there is no room for an accumulation of undigested pollen husks.

This change which is made in the diet explains a point that has been apparently made practical use of in the lucrative trade in queen bees. This is, that if the queen is removed, a new queen is raised by enlarging the cell and altering the food of a working larva. If the working larva has, however, passed the fourth day, that is has begun to receive inferior food, it is impossible or difficult to rear a queen from it. (*American Bee Journ.*, 1880, 550.) W. D. H.

Influence of Food on the Composition of Butter. By E. F. Ladd (*Bied. Centr.*, **18**, 476—480; from *Agricult. Science*, **2**, 251—256).—The experiments were made with two Jersey and two native cows. The foods employed were hay, coarse ground rye, linseed cake, and wheat-bran. Tables are given showing the amounts and composition of foods consumed, yield and composition of milk and composition of the butter. The coarse ground rye and the wheat-bran gave almost the same results, whilst linseed cake distinctly influenced the composition of the butter, giving rise to an increase of 3·5 per cent. of oleïn. N. H. M.

Action of Carbohydrates on the Animal Organs. By P. Albertoni (*Chem. Centr.*, 1889, 608—609, from *Ann. Chim. Farm.*, **9**, 65—88).—Experiments made both on man and on lower animals with a view to determine the action of the carbohydrates, glucose, maltose and saccharose on the animal economy, showed that their absorption into the blood is attended by an increased action of the pulse, to the extent of 15—20 beats per minute in the case of the dog, and from 6—8 beats in the case of a man. The pressure of the blood is also increased by about 15—20 mm. of mercury, and an increased action of the heart also attends the effects; the blood-vessels are enlarged and an increased quantity of blood, about double the normal, flows from them, and the rate of circulation is also much increased. Morphine and chloral prevent the action of the carbohydrates on the circulation.

The author draws the conclusion that the carbohydrates are not to be viewed as a feeding material, but rather that they have an important effect on the action of the heart. J. W. L.

Hæmoglobin in Blood passing to and from the Liver and Spleen. By M. v. Middendorff (*Chem. Centr.*, 1889, 726—727, from *Centr. Physiol.*, 1889, 752—754).—Experimenting with cats, the author found in seven instances that the venal blood of the liver was richer in hæmoglobin, and in other six instances poorer than the blood of the vena portæ. Of the blood of the major mesenteric vein, and that of the vena portæ, the latter was found in all of three instances to contain a larger amount of hæmoglobin, the average being an excess of 6 per cent. Of the blood of the spleen, that taken from the gastrolienalic vein was found to be richer in hæmoglobin and mineral matter than the arterial blood. J. W. L.

Myohæmatin. By C. A. MacMunn (*Zeit. physiol. Chem.*, **13**, 497—499).—A reply to the criticisms of Levy (this vol., p. 633).

Diamines (Ptomaïnes) in Cystinuria. By L. v. Udránszky and E. Baumann (*Zeit. physiol. Chem.*, **13**, 562—594).—A number of cystin calculi were removed by operation from a patient; during the year subsequent to the operation, the urine was examined, at intervals, and was found always to contain a certain quantity of sediment consisting of cystin crystals.

During this time, also, diamines were found in the same urine; these belong to the class of substances called ptomaïnes, and the names cadaverine and putrescine were given to them by Brieger. Cadaverine, $C_5H_{14}N_2$, is identical with pentamethylenediamine (Ladenburg, Abstr., 1887, 125), and putrescine, $C_4H_{12}N_2$, is no other than tetramethylenediamine (this vol., p. 33). These substances were precipitated as benzoyl-compounds from the urine (Abstr., 1888, 1296), and then separated from one another by their different solubilities in ether and alcohol.

Of the two alkaloïds present in the urine, cadaverine was the more abundant. The quantity per diem varied very much; on one occasion, 0·24 gram of benzoyltetramethylenediamine and 0·42 gram of benzoylpentamethylenediamine, and on some other occasions the merest traces were obtained.

Dupré and Bence Jones (*Proc. Roy. Soc.*, **15**, 73) were the first to find an alkaloïd substance in urine. Since then, the question has been often discussed whether the ptomaïnes formed by putrefaction in the alimentary canal are partly reabsorbed and excreted in the urine; and although no observers (except Pouchet, *Compt. rend.*, **98**, 1560) have been able to isolate such substances from the urine, many authors have ascribed the poisonous action of normal and pathological urine to their presence. Stadthagen (*Zeit. klin. Med.*, **15**, Parts 5 and 6) has settled the question by showing that the poisonous substances in urine are inorganic potassium salts.

Certainly diamines are absent both in normal urine and fæces; they are also absent in cases of acute and chronic cystitis, and in the urine of patients suffering from scarlatina, diphtheria, typhoid, pneumonia, peritonitis, and other suppurative processes. The urine and the blood of dogs contain no diamines.

Brieger has shown that diamines are, however, formed in certain putrefactive processes, especially in cultivations of the cholera-bacillus, and the Finkler-Prior vibrio (*Berl. klin. Woch.*, 1887, No. 44). The odour of cholera stools is undoubtedly due to pentamethylenediamine.

In two other cases of cystinuria Stadthagen and Brieger have found diamines in the urine, chiefly pentamethylenediamine (*Arch. pathol. Anat.*, **115**, Part 3).

Cholera and cystinuria have this one circumstance in common—the formation of diamines; and in both cases there is but little doubt that they are formed by the agency of microbes. The fæces of the patient with which the present communication is more particularly concerned were examined, and about 0·5 gram per diem of the two bases was obtained, the tetramethylenediamine being by far the more abundant; this is the opposite to what is found in the urine. This is, however, what would be expected; Brieger showed that where diamines are produced, first pentamethylenediamine, and in the later stages of putrefaction tetrametylenediamine are formed. The penta-compound is here no doubt produced in the small intestine, absorbed, and then excreted in the urine; the tetra-compound is not formed until the large intestine is reached, and so is found in greater abundance in the fæces. Diamines are absent in normal fæces, and in the stools of patients suffering from intestinal obstruction, typhoid, tubercular ulceration of the intestines, &c. Brieger and Stadthagen found diamines in the stools in their two cases of cystinuria.

The absence of a characteristic odour in cases of cystinuria is due to the great dilution in the urine and fæces, or to the acid reaction of these materials, or it may be that the bases are not free but present in combination. More information is, however, still wanting as to the quantity of diamines present in cholera, and researches on the effect of feeding animals on diamines are in progress.

Researches on the amount of ethereal hydrogen sulphates in the urine of the same patient showed that their amount and relation to total sulphates was approximately normal; this shows that the bacteria which produce the diamines are not those that produce the usual putrefactive changes in the alimentary canal.

By distilling albumin and peptone with alkalis, no trace of a diamine is discoverable. Only one product of metabolism is hitherto known which stands in a near relationship to them. This is the ornithine (diamidovaleric acid) of Jaffe (Abstr., 1878, 584 and 585). Brieger (*Berl. klin. Woch.*, 1887, No. 44) and Bocklisch (Abstr., 1887, 742) showed that diamines appear in putrefying liquids after a long time, and that they are probably formed by oxidation processes from monamines. But they appear much more quickly in cultivations of the cholera-bacillus, and are probably really products of the metabolic activity of these organisms.

If the formation of diamines in the alimentary canal of patients suffering from cystinuria is found to be constant, it may ultimately turn out that cystinuria or diaminuria is an infectious disease. The bacteria, however, differ from most pathogenic bacteria in their prolonged existence in the same individual, in this case they must have been present in the intestine for at least a year.

These diamines are both poisons (for symptoms see v. Behring, *Deut. med. Woch.*, **14**, No. 24; Scheuerling, *Maly's Jahresb.*, 1887, 491; Fehleisen and Grawitz, *Virchow's Archiv*, **110**, 1); and the symptoms they produce are very similar to some of those of cholera (hæmorrhages and necrosis); but the muscular cramps and other prominent symptoms of that disease are doubtless produced by other poisonous alkaloïds (toxines, Brieger) not yet separated. The absence of any local action of the diamines on the intestines in cases of cystinuria is probably due to the same cause as the absence of odour, namely, that the free bases are absent, but are in the form of salts.

In this case of cystinuria, cystin was not present in the intestinal contents. W. D. H.

Relation of Ptomaïnes to Infectious Fevers. By A. P. Luff (*Brit. Med. J.*, **2**, 1889, 193—194).—This preliminary communication states that in one case of typhoid fever, and in the urine collected from a number of scarlet fever patients, small quantities of alkaloïds of doubtful nature were obtained. W. D. H.

Proteïd Poisons. By S. Martin (*Brit. Med. J.*, **2**, 1889, 184—187). —It has now been established that certain proteïds are poisonous, but there are no chemical reactions that distinguish them from the non-poisonous proteïds. A list of the poisonous proteïds is as follows:—

Animal.	*Vegetable.*
Snake poison.	Jequirity.
Serum albumin of fishes (eel, &c.)	Papaïn.
Albumoses and peptones.	Lupinotoxin (?).
Proteïds found in certain spiders.	
Wooldridge's tissue-fibrinogens.	

It is, however, with the poison of jequirity (*Abrus precatorius*) that this communication is more particularly concerned. This substance is employed in ophthalmic surgery to produce inflammation of the conjunctiva. Bacteria and alkaloïds were carefully excluded, and the poisonous properties were found to reside in the proteïds, of which there are two—a globulin and an albumose.

The globulin is soluble in a 15 per cent. sodium chloride solution; it coagulates between 75° and 80°; it is precipitated by saturating its solution with sodium chloride or magnesium sulphate. It belongs to the class of vegetable paraglobulins (Abstr., 1887, 507). The albumose is soluble in water, is not precipitated by boiling; it gives the characteristic nitric acid reaction of albumoses, and the "biuret" reaction.

Both these proteïds produce nearly the same effects, namely, local œdema and ecchymosis at the seat of inoculation, with ecchymoses in the serous membranes, and gastro-enteritis, the blood in many cases remaining fluid. There is a gradual sleepiness, ending in coma, and rapid onset of *rigor mortis*. Both proteïds have a remarkable lowering effect on the body temperature; the globulin produces rapid breathing, whilst the albumose does not have this effect to the same degree.

The activity of both proteïds is destroyed at a temperature below the boiling point of water; the globulin between 75° and 80°, the albumose at 85°; temperatures below these points and above 50° diminish the poisonous activity. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Glycerol in Alcoholic Fermentation. By L. v. Udránszky (*Zeit. physiol. Chem.*, **13**, 539—551).—412·6 grams of pure yeast which contained 0·0729 of glycerol (estimated as a benzoyl-compound, Diez) was suspended in 1500 c.c. of water, and alcohol added until the amount present reached 12 per cent. The mixture was kept at 12—16° for 23 days. There was during this time no alcoholic fermentation, no sugar having been supplied to the yeast. The quantity of glycerol now found was 0·1576 gram, an increase of 116·05 per cent.

The above is an instance of the experiments performed in order to solve the question as to the source of glycerol in the alcoholic fermentation of sugar. The conclusion finally drawn is that the newly formed glycerol could only have been derived from the substance of the yeast itself, probably from the lecithin it contains. It must be either a product of the metabolism of the yeast-cell, or is connected with the processes that accompany the death of the cell. Other experiments subsequently showed that on the death of yeast there is a production of glycerol.

It might be said that these experiments do not controvert Pasteur's view that alcohol, carbonic anhydride, glycerol and succinic acid are all derived from the sugar upon which the yeast acts (*Ann. Chim. Phys.* [3], **18**, 323), for it is possible that sugar is formed from the yeast itself, and that this is subsequently fermented. If this was the case, there should be a simultaneous evolution of carbonic anhydride; but this was not the case. The formation of glycerol is therefore not necessarily dependent on the alcoholic fermentation, for it may be formed independently of the production of alcohol, and is derived from the metabolic changes of the yeast-cells themselves.

With regard to succinic acid, no experiments have as yet been made.

W. D. H.

Formation of Sugar and other substances in Yeast. By E. Salkowski (*Zeit. physiol. Chem.*, **13**, 506—538).—Chloroform water (5 c.c. of chloroform shaken with 1000 c.c. of water) is an excellent antiseptic medium (*Deut. med. Woch.*, 1888, No. 16). On digesting yeast with chloroform water (1 part of yeast to 10 of chloroform water), self-fermentation does not occur at the temperature of the air, but the fluid after some days contains sugar, leucine, and tyrosine, and substances of the xanthine-group. The formation of these substances is brought about by a fermentative process, for they are not found in preparations in which the yeast was first sterilised. As the vital processes of the yeast plant are put a stop to by the antiseptic used, the formation of these materials must be the result of the action of a soluble ferment or enzyme.

The sugar which is formed in this way forms a crystalline phenylhydrazine-derivative, melting at 204—205°, reduces Fehling's solution, is readily fermentable with yeast, and is lævorotatory. The quantity of sugar amounted in the mean of 11 experiments to 6·48 per cent. of the dry weight of the yeast used, the minimum being 4·24, and the maximum 8·81. It originates from the carbohydrate constituents of the yeast-cells. There is also in self-fermentation a diminution of the carbohydrates originally present.

With regard to the xanthine present, nearly all the nucleïn of the yeast is decomposed, and the xanthine formed is directly precipitable by silver solution. If the yeast be previously sterilised, the xanthine is present in smaller quantity in the extract, and is not directly precipitable by silver solution, but only after boiling with acids.

W. D. H.

Oxidation in the Living Cell. By PFEFFER (*Ann. Agronom.*, **15**, 234—236).—A dilute solution (1 : 100 or 1 : 1000) of hydrogen peroxide permeates the protoplasm in the cell sap without interfering with the life of the cell. After immersion in this liquid, many tissues, such as the roots of a bean or the root-hairs of *Trianœa bogotensis*, become coloured red or brown, showing that the chromogenous substance has undergone oxidation; also some coloured tissues, like staminal hairs of *Tradescantia* rapidly lose their colour, which is destroyed by oxidation. From these and similar experiments, the author argues the absence of hydrogen peroxide, ozone, or nascent (atomic) oxygen, from the cell contents, and that respiration is carried on by ordinary oxygen. Also the oxygen disengaged by green cells in sunlight is not active, for living *Spirogyra* may be exposed to sunlight in very weak potassium iodide and starch without causing any coloration.

J. M. H. M.

Reduction of Silver Nitrite by the Living Cell. By PFEFFER (*Ann. Agronom.*, **15**, 236—238, from *Flora*, 1889, 46—54).—The author combats the view of Lœw and Bokorny that this reduction is a special property of the living cell, and due to the "active albumin" in it. He cites the facts that many plants fail to give the reaction, that in some cases ebullition does not prevent it, that in *Spriogyra* the reduction does not take place until long after the cells are dead. To explain those cases, where living cells effect the reduction and the same cells dead refuse to do so, the author points out that if the reaction be simply due to some reducing agent dissolved in the cell sap, then on the death of the cell the sap easily diffuses into the ambient water and carries away the reducing substance. Plugging a capillary tube with a little swollen gelatin and placing on one side a solution of tannin, and on the other silver nitrate, he shows that the gelatin is coloured brownish-red in zones by the reduced silver, presenting the appearance observed in the active cells.

J. M. H. M.

Solubility of the Constituents of Seeds. By W. MAXWELL (*Amer. Chem. J.*, **11**, 354—357; compare Abstr., 1888, 170).—The author experimented on the seeds of *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, as follows:—50—100 grams were treated with diastase solution (as a substitute for ptyalin) until free from starch, washed, dried and weighed. Of the residue, one weighed portion (2 grams) was treated with pepsin solution, and another weighed portion with pepsin and trypsin solutions consecutively; the residue in each case was washed, dried, weighed and the nitrogen determined in it by Kjeldahl's method. The following table gives the main results in percentages on the material dried at 100°.

	Dissolved by			Nitrogenous matter in		
	Diastase.	Pepsin.	Pepsin and Trypsin.	Original material.	Pepsin residue.	Pepsin and trypsin residue.
Pisum sativum	58·87	24·87	5·99	4·151	0·143	0·091
Faba vulgaris......	57·39	24·77	3·65	4·477	0·239	0·160
Vicia sativa.......	56·23	28·96	2·04	5·039	0·291	0·255

When *Faba vulgaris* was treated with pepsin, without previous treatment with diastase, only 32 per cent. of the total seed matter was dissolved, and of this 25·33 per cent. consisted of albuminoïds.

In the common methods of determining albuminoïds, the nucleïns, being insoluble in water, are estimated as albuminoïds, which are therefore too high.

Comparison of results obtained by artificial digestion with trials with living animals confirms the value of laboratory experiments.

A. G. B.

Fatty Oil of Cyperus Esculentus. By C. Hell and S. Twerdomedoff (*Ber.*, **22**, 1742—1745).—The tubers of *Cyperus esculentus*, the so-called earth-almond, contain, besides sugar, a considerable quantity (27·1 per cent.) of a fatty oil which can be isolated by extracting with light petroleum. (Compare Munoz y Luna, *Annalen*, **78**, 370.) The crude product is yellowish and has a smell something like that of burnt sugar. When cooled below 0°, a small quantity of solid glycerides separates but immediately redissolves when the temperature is raised. The crude oil was saponified with alcoholic potash, and the resulting soap, after being purified by dissolving it in water and reprecipitating with sodium chloride, was decomposed with lead acetate. The mixture of lead salts obtained in this way was boiled with ether; the extract was proved to contain oleic acid, but no other acid of the same series, whilst the residue, which formed only a small proportion of the mixture, consisted entirely of lead myristate or contained only very small quantities of other fatty acids. These experiments show that the fatty oil of *Cyperus esculentus* consists principally of the glyceride of oleic acid, but also contains small quantities of the glyceride of myristic acid.

F. S. K.

Presence of Betaïne and Choline in the Seeds of Vicia Sativa. By E. Schulze (*Ber.*, **22**, 1827—1829).—Ritthausen has shown that vicine and convicine occur in the seeds of *Vicia sativa* (Abstr., 1881, 1158), and the author now finds that betaïne and choline are also present in the proportion of 11 to 12 grams of the former and 3 to 3·5 grams of the latter in 20 kilos. of seed. In one experiment, choline platinochloride was obtained crystallised in octahedra instead of the ordinary orange-red prisms. W. P. W.

Percentage of Carbonic Anhydride in the Air of Soils. By E. WOLLNY (*Landw. Versuchs-Stat.*, 1889, 197—214).—This is a continuation of previous experiments (*Landw. Versuchs-Stat.*, 1880, 373—391) in which it was shown that the formation of carbonic anhydride was hindered by the presence of vapour of chloroform, whereby the organisms which produce that gas were more or less destroyed. These statements have also been corroborated by Dehérain, who however, states his belief that oxidation proceeds in addition as a purely chemical process. Wollny did not consider this conclusion was justified by the results, and so has undertaken new experiments with a view to settle the question, the action of heat and mercuric chloride being employed as antiseptics, and every precaution taken to ensure accuracy. The results obtained may be thus expressed: the amount of organic matter in the soil is no indication of the quantity of carbonic anhydride when the organic matter is in excess; the percentage of carbonic anhydride is only proportional to the amount of organic matter when this is in small quantities, but when present in greater amounts, then the carbonic anhydride does increase, but to much less an extent, for the larger or smaller quantity of this gas in the air of the soil more or less reduces the activity of the organisims by whose agency the oxidation is produced. Water and temperature have a greater influence on the oxidation, and act in an opposite direction to that of the organic matter; the amount of free gas in the soil affords no indication either of the intensity of the action or for the amount of organic matter.

The addition of liquid manure to the soil results in a reduction of the decomposition of the organic matter when the quantity of the salts therein contained is greater than that already present in the soil, but if the liquid manure is dilute and the absorptive power of the soil for salts is great then the decomposition is promoted. The data on which the author relies for his conclusions are all given in full. E. W. P.

Decomposition of Organic Ammoniacal Compounds in Ensilage. By F. W. A. WOLL (*Landw. Versuchs-Stat.*, 1889, 161—179). —Estimation of albuminoïd and amido-nitrogen has been made in a variety of silages, principally of maize, and the results are given in full detail. It appears that the loss of nutriment by ensiling maize amounts on an average to 24 per cent., whilst the loss of albuminous matter amounts to one-third of the total nitrogenous matter in the original maize; the albuminoïds decrease to 43·91 per cent., whilst the amides rise to 206·7 per cent., which calculated on the dry matter is equivalent to 4·78 and 1·02 respectively. From the evidence produced, it is clear that the loss of nitrogenous matter cannot be referred to decomposition of the ammoniacal compounds, but is due purely to the fermentation which occurs in the silo; further, this loss is in no way obviated by any amount of care which may be taken in the drying of the silage. E. W. P.

Analytical Chemistry.

Simultaneous Estimation of Hydrogen and Nitrogen. By C. GEHRENBECK (*Ber.*, 22, 1694—1696).—By a modification of the open tube Dumas' method of estimating nitrogen, the author is able simultaneously to determine hydrogen. Between the combustion tube and the nitrogen eudiometer, a weighed calcium chloride tube is introduced. The other end of the combustion tube is closed with a cork carrying a three-way cock. One limb of this cock is connected with the carbonic anhydride generator, the other with an oxygen and air supply. The combustion tube is filled exactly as at present, except that care must be taken to mix the substance to be analysed intimately with copper oxide or lead chromate. The operation is first carried out exactly as for a nitrogen determination, but when this is finished, the nitrogen eudiometer is removed, and oxygen, and eventually air, turned on. Of course the carbonic anhydride used must be dried, and it is preferable also to introduce a second (unweighed) calcium chloride tube between the weighed tube and the eudiometer. A number of test analyses have been made with good results. The method is of especial value in conjunction with Messenger's wet method for the estimation of carbon (this vol., p. 80). L. T. T.

Eudiometric Investigation with Mixtures of Ammonia and Oxygen. By S. NEUMANN (*Chem. Centr.* 1889, 754, from *Math. naturw. Ber. ans Ungarn.*, 6, 136—151).—In the case of a mixture of ammonia and oxygen being exploded by passing the electric spark, an amount of ammonia equivalent to the oxygen is burned to nitrogen and water. If the oxygen is in excess, a small part of the nitrogen is oxidised, whilst in the event of the ammonia preponderating, a part of the unburnt ammonia suffers decomposition, owing to the heat of the explosion. If the pressure in the eudiometer be so far reduced that no explosion takes place, the ammonia may be burnt slowly.

J. W. L.

Estimation of Hydrogen Sulphide in Aqueous Solution. By G. FAUSER (*Chem. Centr.*, 1889, 754—755, from *Math. naturw. Ber. ans Ungarn.*, 6, 154—160).—The hydrogen sulphide, generated from antimony sulphide, was purified from hydrogen chloride by passing it over alum previously saturated with ammonia, and was then passed into freshly boiled water. The vessel containing the aqueous solution stood in another of water, by means of which it could be cooled or warmed as required.

The determination of the hydrogen sulphide is made as follows:—The solution is delivered to the bottom of a flask containing a known quantity of a solution of bromine (prepared by acting on potassium bromate with hydrogen chloride in presence of potassium bromide), an excess of potassium iodide added, and the liberated iodine titrated with sodium thiosulphate. The following table contains the author's results compared with Schönfeld's.

Temperature.	Coefficient obtained by Fauser.	Coefficient obtained by Schönfeld.
0°	4·6582	4·3706
5	4·0407	3·9652
10	3·4775	3·5858
14	3·0674	3·3012
15	2·9902	3·2326
20	2·6105	2·9053

From his own results, the author calculates the following coefficients:—3° = 4·4109, 4° = 4·2630, 5° = 4·1206, 6° = 3·9836, 7° = 3·8521, 8° = 3·7261, 9° =3·6056, 10° = 3·4906, 11° = 3·3810, 12° = 3·2769, 13° = 3·1783, 14° = 3·0852, 15° = 2·9976, 16° = 2·9154, 17° = 2·8387, 18° = 2·7675, 19° = 2·7018, 20° = 2·6416, 21° = 2·5868.

J. W. L.

Detection of Phosphoric Acid of Mineral Origin. By J. STOCKLASA (*Bied. Centr.*, **18**, 444—446).—Experiments made with various phosphates of animal and mineral origin show that v. Lorenz's reaction (*Bied. Centr.*, **18**, 130) is not always trustworthy.

N. H. M.

New Apparatus for the Indirect Estimation of Carbonic Anhydride. By E. SACK (*Ber.*, **22**, 1007—1009).—The author describes, with the aid of a diagram, a new form of apparatus for the indirect estimation of carbonic anhydride. No stopcocks are employed, and the apparatus is more stable and more easily washed than the ordinary form.

F. S. K.

Reduction of Barium Sulphate to Barium Sulphide on Ignition with Filter-paper. By C. W. MARSH (*Chem. News*, **59**, 309—310).—In a number of experiments, barium sulphate was ignited with the filter-paper, and after weighing, the ignited mass was treated first with water then with dilute hydrochloric acid. The solution, if it contained hydrogen sulphide, was treated with bromine, and then boiled to drive away excess of bromine, any barium in solution would be derived from barium sulphide in the ignited barium sulphate, and was estimated in the usual manner. In this way the author has proved conclusively that a considerable proportion of the barium sulphate may be converted into barium sulphide during ignition with filter-paper, the quantity being less when the ignition is conducted in an open crucible. It is therefore always desirable to treat the ignited mass with sulphuric acid and re-ignite. Hydrogen sulphide can sometimes even be detected on adding water to the mass after ignition with filter-paper.

D. A. L.

Estimation of Calcium and Magnesium in Gun-cotton. By H. SCHIERNING (*Chem. Centr.*, 1889, 649, from *Tidsskr. Ph. Ch.*, 1888, 353).—3 to 5 grams of the gun-cotton are saturated in a crucible with a mixture of equal parts of ether and alcohol in which paraffin has been dissolved, and to which one-fourth of its volume of water is added. A small piece of paraffin is added to the mixture, and the mass is set on fire. The carbonised mass is then completely incinerated over the blast lamp. The ash is dissolved in standard hydrochloric acid, ammonium chloride added, and a known quantity of standard sodium hydroxide solution added in excess. The insoluble oxides of iron and aluminium and the silica are filtered off and weighed, whilst the dissolved magnesia and calcium oxide are estimated by titrating back again. J. W. L.

Electrolytic Separation of Cadmium from Zinc. By E. F. Smith and L. K. Frankel (*Amer. Chem. J.*, **11**, 352—353).—The authors find that, by carefully regulating the current, cadmium may be separated from zinc in alkaline cyanide solution. In the first series of seven experiments, 0·1817 gram of cadmium was present in each case, together with 0·2 gram of zinc in three cases; in the second series of nine experiments, 0·2426 gram of cadmium was present in each case together with 0·2 gram of zinc in six cases. In all the experiments, 4·5 grams of potassium cyanide and 200 c.c. of water were used; the current evolved 0·3 c.c. of water-gas per minute (?); and the time varied from 18 to 23 hours; in a longer time, the zinc begins to deposit with the cadmium. The errors in determining the cadmium varied from —0·27 to +0·60 per cent. of the amount present. A. G. B.

Hampe's Method for Estimating Cuprous Oxide in Metallic Copper. By E. P. Dewey (*Chem. Centr.*, 1889, 707, from *J. anal. Chem.*, **3**, 33).—Having prepared a mixture of cuprous oxide and metallic copper, the author found that it contained 98·12 copper, 0·013 iron, and 1·867 oxygen per cent. which corresponds with 83·317 copper, 16·670 cuprous oxide, and 0·013 iron. Applying Hampe's method to the estimation of this mixture, 24·44 per cent. cuprous oxide was found, whereas calculating (as the author suggests should be done) that all the copper in the form of the suboxide is precipitated as basic nitrate, 16·29 per cent. is found. As he, however, determined the composition of his mixture of copper and suboxide by taking the difference as equal to oxygen, there is some doubt as to the validity of his conclusion. J. W. L.

Volumetric Estimation of Nickel. By F. Moore (*Chem. News*, **59**, 292—293; compare this vol., p. 747).—The author finds that large quantities of ammonium salts and the presence of manganese interfere with the accuracy of the method of estimating nickel recommended by him (*loc. cit.*). The following process is not affected by iron, aluminium, zinc, and small quantities of manganese. Excess of sodium pyrophosphate is added to the slightly acid solution until the precipitate first formed redissolves, the solution is made slightly acid with hydrochloric acid, then distinctly alkaline with ammonia. Standard potassium cyanide (containing 22 to 25 grams per litre) is then run in until the blue colour disappears, cupric ferrocyanide is now added either dissolved in ammonium oxalate or as emulsion, and the titration continued in the presence of zinc until this colour disappears or, in absence of this metal, until the yellow colour appears. The results compare well with numbers obtained by electro-deposition.

D. A. L.

Volumetric Estimation of Gases dissolved in Water. By O. PETTERSSON (*Ber.*, 22, 1434—1439).—For the volumetric estimation of gases dissolved in water, the author employs an apparatus, a diagram of which is given, consisting essentially of a glass fractionating flask A, the size of which depends on the quantity of gas in the sample to be examined, connected with a graduated burette-shaped tube B of about 48 c.c. capacity. B is completely surrounded by a larger glass cylinder E, through which cold water can be made to circulate, and the upper extremity projects through the cylinder E and is provided with a stop-cock *z*; the end of B finally becomes wider and serves as a funnel, *t*, for introducing the reagents. The side tube of the flask A is provided with a bulb at the centre and is connected by means of india-rubber tubing with a cylindrical vessel C, of about 250 c.c. capacity. The volume of the whole apparatus (A + B) up to where the cylindrical vessel C joins the india-rubber tubing is ascertained to within 0·5 c.c.

In making an analysis, a fresh sample of the water is mixed with dilute sulphuric acid (10 c.c.) and poured into C (*z* being open) until A and B are completely filled; the tubing at the junction with C is then pinched to, and the excess of water poured out. The water in A is then heated, carefully at first, and finally kept in brisk ebullition for 10 minutes. At the end of the operation, a rapid stream of cold water is passed through E, C is raised until the water in B and C is at the same level, and the volume of the gaseous mixture is noted, the temperature being indicated by a thermometer placed inside E. The carbonic anhydride is then absorbed by pouring a little soda into the funnel *t*, and opening the cock *z* so that some of the liquid flows into B, and the volume of the oxygen is subsequently ascertained by absorption with an alkaline solution of pyrogallol. The residual gas consists of nitrogen alone, or of nitrogen and methane (compare p. 935); in the latter case, the funnel *t* is filled with water, and the gaseous mixture is passed into a suitable apparatus and analysed in the usual manner.

As soon as the water in B is cooled, the carbonic anhydride is, to some extent, absorbed again. This error can be eliminated by reading the volume 5 and 10 minutes after turning on the cold water; the difference gives the volume of carbonic anhydride absorbed in the first five minutes.

Experiments showed that the volume of carbonic anhydride found is 8 to 10 per cent less than the quantity actually present, as the whole cannot be expelled even by the most persistent boiling; if, however, large quantities of sulphuric acid are added, the whole of the gas is driven out.

As the contact of the water in C with the air might, in estimating oxygen and nitrogen, influence the results, the author employed another form of apparatus in which the atmosphere is completely excluded from the sample. The side-tube of the flask A is forked, one limb *x* being connected by india-rubber tubing with the vessel C as before, the other, *y*, with a glass cylinder F, which is connected with a cylindrical reservoir D. The sample is introduced as before, F having been previously filled with mercury up to the fork, and the limb *y* closed with a pinch-cock. The tubing connecting C with the limb *x* is then closed with a pinch-cock close to the fork, *y* is opened and the water in A, and finally also that which has been driven into F, heated to boiling as before. As sulphuric acid must not be added to the water, only oxygen and nitrogen can be estimated with this apparatus. The results are within 0·1 c.c. per litre. F. S. K.

Estimation of Organic Nitrogen in Natural Waters by the Kjeldahl Method. By T. M. DROWN and H. MARTIN (*Chem. News*, **59**, 272—276).—Taking into consideration the variable results obtained by different operators for albuminoïd ammonia in waters, the authors conclude that a simple and accurate method of estimating total organic nitrogen would be generally practised in place of it, and they find the Kjeldahl method answers the purpose well. 500 c.c. of the water is boiled in a round-bottomed, long-necked, 900 c.c. flask until 200 c.c. have distilled off, the "free ammonia" may be determined in this distillate. When cool, 10 c.c. of pure concentrated sulphuric acid is added and the remainder of the water boiled off cautiously, pulverised permanganate is now added (although it is doubtful if this is absolutely necessary) and then 200 c.c. of water free from ammonia. 100 c.c. of a solution, containing 200 grams of sodium hydroxide per litre, and which has been boiled with some permanganate, is run in, the flask adjusted to a tin-tube condenser, well shaken, and the distillation proceeded with. Nesslerising is preferred by the authors to titration. Nitrates and nitrites have not been found to interfere with the accurate determination of organic nitrogen in these waters. Satisfactory results appear to have been obtained with various waters, even in the presence of added nitrates and nitrites. Experimental determinations have also been made with known quantities of ammonia, urea, uric acid, and naphthylamine, but no comparison has been instituted with the Frankland-Armstrong combustion method. D. A. L.

Rapid Method of Analysing Water prior to its Softening for Technical Purposes. By L. VIGNON (*Bull. Soc. Chim*, **50**, 598—604; compare Abstr., 1888, 325).—In order to ascertain the quantities of lime and of sodium carbonate necessary to soften water used for technical purposes, the author proposes to titrate 50 c.c. with a standard solution of calcium hydroxide, using alcoholic phenolphthalein (10 drops) as an indicator. By this means, the amount of lime required to combine with the free carbonic anhydride and to precipitate the soluble hydrogen magnesium and hydrogen calcium carbonates is determined. To estimate the amount of sodium carbonate requisite to precipitate salts of calcium and magnesium other than acid carbonates, 100 c.c. of the water is taken and exactly neutralised with the standard calcium hydroxide solution, and the precipitated carbonates are filtered off; to one-half of the filtrate phenolphthaleïn is now added, and sodium carbonate solution containing 1 gram per litre is run in until the reddening of the indicator is persistent.

The method is not very accurate in the presence of considerable quantities of magnesium sulphate or chloride. T. G. N.

Estimation of Benzene-vapour in Coal-gas. By BERTHELOT (*Bull. Soc. Chim.*, **50**, 660—662).—The author refers to his discovery in 1876 that the illuminating power of the Paris gas is largely due to the presence of benzene-vapour (compare Abstr., 1876, ii, 183, and 1877, ii, 447). To determine the amount of benzene-vapour in coal-gas by volumetric absorption, 20—25 c.c. of the gas measured over water is to be briskly agitated in a small flask with 1 c.c. of fuming nitric acid for half a minute at the most before final measurement. These conditions must be strictly observed, for otherwise the oxidisable gaseous constituents are attacked, a circumstance, which the short period of contact with the acid, diluted as it is by the water moistening the walls of the vessel, almost entirely negatives, and sufficiently correct results are obtainable. (*Vide Ann. Chim. Phys.* [6], **12**, 296.) T. G. N.

Estimation of Sugar by Fehling's Solution. By H. CAUSSE (*Bull. Soc. Chim.*, **50**, 625—626).—The author suggests the addition of 4 c.c. of a 5 per cent. solution of potassium ferrocyanide and 20 c.c. of water to each 10 c.c. of Fehling's solution employed. On running in the sugar solution to the boiling mixture, the potassium ferrocyanide dissolves the cuprous oxide as quickly as it is precipitated and forms a colourless solution, thus rendering the exact point of decolorisation more easily seen and preventing bumping.

Potassium ferrocyanide appears to be without action on hot or cold Fehling's solution. On cooling the liquid obtained, after titration, it turns brown and deposits colourless crystals which the author intends to study. T. G. N.

Tin in Sugar. By T. L. PHIPSON (*Chem. News*, **59**, 255—256).—Tin chloride appears to be used for giving some classes of sugar a golden hue, a practice which, owing to the quantities employed, is objectionable, inasmuch as it has been shown that tin chloride is poisonous. This adulteration is estimated by dissolving the sugar in a large excess of water without separating any of the residue, acidifying with hydrochloric acid, treating with hydrogen sulphide, allowing to remain at least 48 hours, then washing out the precipitate with ammonium sulphide, reprecipitating with just sufficient hydrochloric acid, and ultimately weighing as oxide. D. A. L.

Estimation of Formaldehyde. By G. LOSEKANN (*Ber.*, **22**, 1565—1566).—In the titration of formaldehyde by Legler's method (Abstr., 1883, 1035), the reaction is that expressed by the equation $6H{\cdot}COH + 4NH_3 = (CH_2)_6N_4 + 6H_2O$. The hexamethyleneamine thus formed is mono-basic, and neutralises one equivalent of acid. In calculating the results, therefore, 6 mols. of formaldehyde were present for every 3 mols. of ammonia seemingly used up, instead of for every 4 mols. as stated by Legler. L. T. T.

Estimation of Fatty Acids from Butter. By R. Wollny (*Chem. Centr.*, 1889, 397, from *Milch Zeit.*, **17**, 527).—6·25 grams of butter-fat is weighed in an Erlenmeyer flask of 300 c.c. capacity. 25 c.c. of alcoholic potash, which is equal to 73—74 c.c. of N/2 sulphuric acid, is added, and the flask closed with a good stopper through which passes a tube, 10 mm. wide by 50 mm. long. The flask and contents are now heated for 20 minutes by means of a small flame which must not bring the soap solution to boiling. The flask is next cooled, and 150 c.c. of boiled, distilled water added. After complete solution of the soap, the solution is cooled to 15°, and 75 c.c. N/2 sulphuric acid added. The flask is closed with a stopper, and the contents shaken briskly for a minute, when the insoluble fatty acids will form a curdy precipitate, and will allow of the ready filtration of the solution, of which latter 200 c.c. is filtered off and titrated with barium hydroxide solution. A blank experiment made in exactly the same manner, only with the omission of the fat, determines the amount of sulphuric acid added in excess of the alcoholic potash. From the amount of barium hydroxide solution used, the amount of fatty acids soluble in dilute alcohol may be calculated. J. W. L.

Estimation of Fat in Milk. By P. G. Short (*Bied. Centr.*, **18**, 416—417).—20 c.c. of well-mixed milk is shaken in a tube with 10 c.c. of a solution of 250 grams of soda and 300 grams of potash in 1800 c.c. of water. The tubes used are of glass $\frac{1}{16}$th of an inch thick; the lower half, 5 inches long, is $\frac{15}{16}$ inch in diameter, the upper half has an internal diameter of $\frac{1}{4}$ inch. A number of such tubes containing the mixture of milk and alkali is heated in a suitable water-bath until all the mixtures are uniform, which requires 1 to 2 hours. The tubes are then allowed to cool to 65°, and to each, 10 c.c. of a mixture of sulphuric and acetic (sp. gr. 1·047) acids (equal vols.) is gradually added. The acid is mixed with the milk by blowing air through by means of a thin, glass tube. The tubes are again heated in boiling water for an hour, then filled up to an inch from the top with hot water, and put back into the hot, but not boiling, water, and kept there for an hour, after which they are taken out and allowed to cool. The layer of fat is then measured with a millimetre measure, and the percentage of fat calculated by means of the formula $100\frac{a \times b \times c}{d \times e}$, in which a is the length of the column of fat, b the value of 1 mm. in cubic centimetres, c the sp. gr. of the insoluble fatty acids × 100(= 914), d the weight of the 20 c.c. of milk, and e the percentage of insoluble, fatty acids in the butter fat.

The method is easily performed, and gives more concordant results than the lactobutyrometer. N. H. M.

Free Alkali of Soap. By J. A. Wilson (*Chem. News*, **59**, 280).—The author points out difficulties in the estimation of free alkali in soap which contains both free glycerides and free alkali (this vol., p. 448). Neither the brine nor carbonic anhydride methods are trustworthy, and when palm-nut or cocoa-nut oil has been used in making the soap, titration with soda is inaccurate for ascertaining the amount required to neutralise the fatty acids. Results with various soaps are given, showing discrepancies between numbers obtained for alkali by titration and for alkali by titration of the insoluble fatty acids, and by alcohol test. Calico printers' soap generally contains excess of acid, which must be taken into consideration when titrating.

D. A. L.

Estimation of Aniline and Methylaniline. By F. Reverdin and C. de la Harpe (*Ber.*, **22**, 1004—1006).—The methods at present employed for the quantitative analysis of a mixture of aniline, methylaniline and dimethylaniline are not sufficiently exact, but by the process described below the three bases can be accurately estimated.

The aniline is first estimated by means of a standard solution of salt-R, 1 litre of which is equivalent to about 10 grams of naphthol. 7—8 grams of the basic mixture is dissolved in 28—30 c.c. of hydrochloric acid and the solution made up to 100 c.c. with water; 10 c.c. of the resulting solution is diluted with water and ice, and diazotised with a quantity of sodium nitrite equivalent to the quantity of basic mixture present—supposing it to consist of aniline alone. The whole is then poured into a known volume of the standard salt-R solution, previously mixed with excess of sodium carbonate, and the dye which is formed is precipitated with sodium chloride. The filtrate is then tested with diazobenzene and salt-R solution to ascertain which compound is present in excess, and by repeated experiments the volume of the standard solution required to exactly precipitate the diazobenzene is accurately determined. A mixture containing 10·76 per cent. of aniline gave 10·24—10·40 per cent.

1—2 grams of the basic mixture placed in a flask provided with a reflux condenser is mixed as quickly as possible with a known quantity (2—4 grams) of acetic anhydride, kept for half an hour at the ordinary temperature, then about 50 c.c. of water added, and the whole boiled for 45 minutes to decompose the excess of acetic anhydride. The cold solution is diluted to a known volume, and the acetic acid estimated by titrating with sodium carbonate, phenolphthaleïn being used as indicator. If the excess of acetic anhydride together with the quantity necessary to combine with the aniline (which has been previously determined) is subtracted from the weight of acetic anhydride taken, the difference gives the quantity of anhydride which has combined with the methylaniline. The analysis of a mixture containing 10·42 per cent. of aniline, 10·97 per cent. of methylaniline, and 78·61 per cent. of dimethylaniline gave 10·30, 11·16, and 78·54 per cent. respectively.

In estimating methylaniline as methylphenylnitrosamine, varying quantities of nitromethylphenylnitrosamine, and sometimes also of paranitrodimethylaniline are formed according to the conditions of the experiment, the former being produced in large quantities when excess of sodium nitrite is added to a cooled solution of methylaniline hydrochloride. The nitrosonitrosamine can be distinguished from its oxidation product by a reaction which is doubtless generally applicable to the detection of paranitroso-derivatives as well as nitrosamines and nitramines. A 50 per cent. acetic acid solution of the substance to be investigated is heated for some hours on the water-bath with gallic acid; if a nitrosonitrosamine be present, the gallocyano-reaction is produced, though only slowly, whilst the nitronitrosamine is without action, and the solution remains yellow.

Phenylmethylnitrosamine solidifies at 2°, or sometimes at an even higher temperature to moss-like needles which melt at about 12—15°.

Small quantities of tetramethyldiamidodiphenylmethane are formed when dimethylaniline is kept for a long time at the ordinary temperature with excess of acetic anhydride, but when it is warmed for several hours with anhydrous acetic acid considerable quantities (10—15 per cent.) of tetramethyldiamidodiphenylmethane are formed.

When aniline is boiled for two hours with excess of acetic anhydride, diacetanilide is probably formed, but when aniline and methylaniline are treated with cold acetic anhydride the monacetyl-derivatives are alone produced, and the reaction is at an end in a very short time, no secondary products being formed. F. S. K.

The Knop-Hüfner Method of Estimating Urea. By R. LUTHER (*Zeit. physiol. Chem.*, 13, 500—505).—In the quantitative estimation of urea by means of sodium hypobromite, a part of the nitrogen remains behind, and does not pass into the collecting tube. Part of this is oxidised to form nitric acid; another part remains unoxidised, and is present in such a form that on boiling with alkalis it is evolved as ammonia.

Fauconier (Abstr., 1880, 513) was the first who pointed out that nitric acid was formed; according to the method he employed, however, he did not exclude the possibility of its formation by the action of potassium chlorate from unaltered urea, or a cyanate. In the present research the following method was employed: Urea was warmed with excess of barium hypobromite until gas ceased to come off; silver sulphate in excess was added to the liquid, by which means silver bromide, bromate, and oxide, barium sulphate, and perhaps some bromate were precipitated. Barium hydroxide was then added; silver oxide and barium sulphate were thus precipitated; excess of barium hydroxide was precipitated by carbonic anhydride and filtered off. The filtrate contained now only barium nitrate, the estimation of which showed that at least 3—4 per cent. of the nitrogen of the urea had been oxidised to form nitric acid. This source of error can, however, be avoided by the addition of glucose to the solution of urea, as it reduces nitric acid *in statu nascenti*.

There appears, however, to be no means of preventing the loss of the remainder of the nitrogen. The nitrogen which is contained probably either as a cyanate, or cyanurate, or as a compound with sodium bromide or bromate, is driven off as ammonia on heating with alkali. The loss of nitrogen in this way amounts to about 1·5 per cent.

The amount of these losses varies, however, with the concentration, temperature, presence of other substances in solution, and so forth; rendering the hypobromite method of estimating urea accurately, therefore, a most uncertain one. W. D. H.

Estimation of Uric Acid in Human Urine. By W. CAMERER (*Zeit. Biol.*, **26**, 84—111).—The different methods which have been proposed by Salkowski, Ludwig, Haycraft, &c., are described and compared with one another in series of experiments with solutions of uric acid and with urine. As a result of these investigations, the following method is proposed:—The urine for the 24 hours, as fresh as possible and preferably free from deposits, is mixed with a measured quantity of sodium hydroxide solution: the solution used should be from 0·4 to 1 gram to 500 c.c. of water. This causes a precipitate of phosphates: the uric acid remains in solution. The mixture is then brought to sp. gr. 1·010—1·011 by the addition of water. If, however, the urine is rich in uric acid, the dilution must be greater; if poor, less. The urine in the first four hours after a meal contains nearly twice as much uric acid, and the urine of leucæmic patients twice or three times as much as the day's urine of a healthy man. The night's urine is poor in uric acid. To 300 c c. of the diluted urine, 50 c.c. of magnesia mixture is added. The magnesia mixture used is that recommended by Salkowski (*Pflüger's Archiv*, **5**, 319), and consists of 1 part of crystalline magnesium sulphate, 2 parts of ammonium chloride, 4 parts of ammonia (sp. gr. 0·924), and 8 parts of water. The precipitate so produced is filtered off. The first 30 c.c. is used for washing the measuring glass, the next 175 c.c. is used for analysis. It is placed in a beaker containing about 0·5 gram of finely divided calcium carbonate, and then about 5 c.c. of a 3 per cent. solution of silver nitrate is added. In a few minutes the silver precipitate settles; a little of the clear, supernatant fluid is removed and tested with nitric acid in order to ascertain that it contains silver. The precipitate is collected on a filter. The calcium carbonate prevents any of it passing through the filter. It is washed free from silver and chlorides, and dried. It is then placed in a combustion-tube and a nitrogen estimation made by Kjeldahl's method. From this, the quantity of uric acid is calculated.

In a previous communication, the relation of total nitrogen to the nitrogen from the urea was investigated (Abstr., 1888, 518); the difference is due to nitrogen from substances like uric acid, creatinine, &c., grouped together under the term extractives. It is now found that in the 24 hours' urine the relation of the nitrogen from uric acid to that in the total extractives is 1 : 7·4. W. D. H.

Van Deen's Test for Blood and Vitali's Test for Pus. By E. v. BRÜCKE (*Monatsh.*, **10**, 129—143).—The author discusses the views of several investigators and gives minute directions, derived from their and his own observations, for the best methods of applying Van Deen's and Vitali's tests with tincture of guaiacum and turpentine oil. G. T. M.

General and Physical Chemistry.

Crystalline Form of Grape-sugar and of Optically Active Substances in General. By F. Becke (*Monatsh.*, 10, 231—232).—Optically active substances cannot form crystals which possess either a plane of symmetry or a centre of symmetry. Investigations on the crystalline form of grape-sugar did not show the hemimorphism which, theoretically, was to be expected, but the crystals of the hydrate, $C_6H_{12}O_6 + H_2O$, are hemimorphous; the elements are $a : b : c = 1·7350 : 1 : 1·9080$ $\beta = 97° 59'$. Anhydrous grape-sugar crystallises in rhombic, hemihedric forms, and the axial relationship is $a : b : c = 0·704 : 1 : 0·335$. A certain relationship between the two forms is shown by the existence of a zone with angles of about 60° in both: hydrate $1\bar{1}0.\bar{1}\bar{1}0 = 60° 24'$, anhydrous substance $\chi(111).\chi(\bar{1}\bar{1}1) = 60° 26'$. F. S. K.

Electrical Behaviour of Platinum in Persulphuric Acid, and the Galvanic Polarisation in the Formation of the Latter. By F. Richarz (*Zeit. physikal. Chem.*, 4, 18—30).—The polarisation in the electrolysis of dilute sulphuric acid, which is due to the formation of persulphuric acid, ozone, and hydrogen peroxide, gives rise to an electromotive force, the amount of which the author endeavoured to determine by that of the element Pt | H_2SO_4,aq | $H_2S_2O_8$,aq | Pt. The formation of oxygen, however, at both plates, and its occlusion, prevented this from being accomplished. In its place were therefore substituted the following comparisons:—

Hg | Hg_2SO_4 | H_2SO_4,aq | $H_2S_2O_8$,aq | Pt = 0·75 Daniel.
Hg | Hg_2SO_4 | H_2SO_4,aq | Pt = 0·09—0·23 „
and Zn | H_2SO_4,aq | $H_2S_2O_8$,aq | Pt = 2·06 „
Zn | H_2SO_4,aq | Pt = 1·31—1·54 „

from which is obtained as a mean value

Pt | H_2SO_4,aq | $H_2S_2O_8$,aq | Pt = 0·61 „

This represents the electromotive force necessary to overcome polarisation in the electrolytic cell. From the heat developed in the reaction $H_2S_2O_8,aq = 2H_2SO_4,aq + O$, the above may also be calculated, and the number 0·56 Dan. was, in fact, thus obtained. The agreement of the calculated and observed values in the above reaction points to the production of persulphuric acid as the primary electrolytic process, and this is further confirmed by the high E.M.F. (greater than that of the Grove's cell) of the element in which zinc and persulphuric acid are employed. H. C.

The Rise in the Zero Point of Mercurial Thermometers made of Jena Glass. By F. Allihn (*Zeit. anal. Chem.*, 28, 435—438).—The variations in the zero point are exhibited most prominently by thermometers made of glass containing both sodium and potassium, glass containing only one of these alkalis being much less subject to the well known variations. Thermometers which show only a small temporary depression of the zero point after heating, generally exhibit the slow permanent rise also to a very small extent. The author has had under observation some thermometers of Jena glass, containing zinc, calcium, sodium and aluminium, and boric and silicic acids. The zero point of each thermometer was observed a few weeks after manufacture, and again after an interval of one to three years. In no case was the rise more than 0·04°, and in some of those kept the longest it was only 0·01° or 0·02°. The temporary depression on sudden cooling after heating for half an hour at 100° is only 0·05° with Jena glass, and disappears in two or three days, whilst with some other glasses it amounts to 0·4°, and lasts for weeks. M. J. S.

Heat of Combustion of Benzene and of other Hydrocarbons of the Aromatic Series. By F. STOHMANN, C. KLEBER, and H. LANGBEIN (*J. pr. Chem.* [2], **40**, 77—95; compare this vol., p. 929). —The authors have redetermined the heat of combustion of benzene, and find that their former value is correct (Abstr., 1886, 409; 1887, 425, 427). They have also determined the following thermal values:—

	Heat of combustion. Calories.	Heat of formation. Calories.
Durene, $C_{10}H_{14}$	1393·9	+29·1
Pentamethylbenzene, $C_{11}H_{16}$...	1554·1	+31·9
Hexamethylbenzene, $C_{12}H_{18}$...	1712·2	+36·8
Diphenyl, $C_{12}H_{10}$	1494·3	−19·8
Naphthalene, $C_{10}H_8$	1233·6	−17·6
Anthracene, $C_{14}H_{10}$	1694·3	−33·3
Phenanthrene, $C_{14}H_{10}$	1693·5	−32·5

The following conclusions may be drawn from these numbers:—

(1.) The heat of combustion of the solid homologue of benzene increases, on an average, 155·1 Cals. for the addition of each methyl-group.

(2.) The substitution of the phenyl-group for hydrogen in benzene, to form diphenyl, increases the heat of combustion by 717·0 Cals.

(3.) The displacement of a hydrogen atom in the hydrogen molecule by the phenyl-group makes the heat of combustion of the benzene molecule thus formed 718·5 Cals. higher than that of the hydrogen molecule.

(4.) The formation of diphenyl from benzene, with separation of two atoms of hydrogen, takes place without any apparent thermal effect.

(5.) The thermal values of anthracene and phenanthrene are practically identical.

(6.) The conversion of benzene into naphthalene and naphthalene into anthracene raises the heat of combustion some 458 Cals. in each case. A. G. B.

Heats of Dissolution and Formation of Hydrated Metallic Chlorides. By P. SABATIER (*Bull. Soc. Chim.* [3], 1, 90—91; compare this vol., p. 1049).—These values are for 1 mol. of salt dissolved in 300 to 600 H_2O.

$CaCl_2,H_2O$ at 21·5°	develops	+11·75 Cal.
$SrCl_2,2H_2O$ at 21·5°	,,	+3·30 ,,
$MgCl_2,5H_2O$ at 19·6°	,,	+6·40 ,,
$\frac{1}{3}(3MnCl_2,5H_2O)$ at 21°	,,	+9·10 ,,
$FeCl_2,2H_2O$ at 20°	,,	+8·70 ,,
$\frac{1}{3}(Fe_2Cl_6,5H_2O)$ at 20°	,,	+14·00 ,,
$CoCl_2,2H_2O$ at 23·5°	,,	+9·85 ,,
$NiCl_2,2H_2O$ at 21·5°	,,	+10·45 ,,
,, at 19·5°	,,	+10·30 ,,

and the heats of dissolution of the above chlorides, whether effloresced or crystallised from hydrochloric acid, correspond.

$Al_2Cl_6,12H_2O$ dissolved in 900 H_2O at 15·5° develops +26·4 cals.

Heat of formation of hydrates which are stable in a dry vacuum. H_2O is calculated as solid.

$CaCl_2 + H_2O$	develops	+4·20 Cal.	each H_2O =	+4·20 Cal.
$SrCl_2 + 2H_2O$	,,	+5·20 ,,	,,	+2·60 ,,
$MgCl_2 + 5H_2O$	,,	+22·30 ,,	,,	+4·40 ,,
$\frac{1}{3}(Al_2Cl_6) + 4H_2O$ ..	,,	+36·60 ,,	,,	+9·1 ,,
$MnCl_2 + \frac{5}{3}H_2O$	,,	+4·5 ,,	,,	+2·70 ,,
$FeCl_2 + 2H_2O$	,,	+6·4 ,,	,,	+3·20 ,,
$\frac{1}{3}(Fe_2Cl_6) + \frac{1}{3}(5H_2O)$	,,	+4·8 ,,	,,	+2·80 ,,
$CoCl_2 + 2H_2O$	,,	+5·7 ,,	,,	+2·85 ,,
$NiCl_2 + 2H_2O$	,,	+5·95 ,,	,,	+2·95 ,,

Heat of formation of hydrates which are unstable in a dry vacuum:—

$CaCl_2,H_2O + 5H_2O$	develops	+9·00 Cal.	each H_2O	+1·8 Cal.
$SrCl_2,2H_2O + 4H_2O$	,,	+4·50 ,,	,,	+1·1 ,,
$MgCl_2,5H_2O + H_2O$	,,	+2·00 ,,	,,	+2·0 ,,
$MnCl_2,\frac{1}{3}(5H_2O) + \frac{1}{3}(7H_2O)$.	,,	+4·20 ,,	,,	+1·8 ,,
$FeCl_2,2H_2O + 2H_2O$	,,	+2·60 ,,	,,	+1·3 ,,
$CuCl_2 + 2H_2O$	,,	+3·70 ,,	,,	+1·8 ,,
$CoCl_2,2H_2O + 4H_2O$	,,	+6·95 ,,	,,	+1·7 ,,
$NiCl_2,2H_2O + 4H_2O$	,,	+5·90 ,,	,,	+1·5 ,,

These thermochemical results are therefore in complete accordance with the relative stability of the hydrates. T. G. N.

Apparatus for Cryoscopical Investigations. By N. v. KLOBUKOFF (*Zeit. physikal. Chem.*, 4, 10—17).—The apparatus in question enables the experimenter to perform a number of successive experiments rapidly and with great accuracy. It is, however, somewhat complicated, and cannot be described without the sketch which accompanies the paper. H. C.

Specific Gravities of Aqueous Solutions. By G. T. GERLACH (*Zeit. anal. Chem.*, **28**, 466—524; see also Abstr., 1888, 894).—The author gives numerous tables of the specific gravities of salt solutions, and deduces the following conclusions from them:—

1. The water of crystallisation of salts always occupies in solution the same volume as an equal weight of solvent water.

2. When a salt crystallises with several proportions of water, the smaller the number of molecules of water of crystallisation, the greater is the space each molecule occupies in the solid form.

3. It would therefore appear that salts in solution are not in combination with water of crystallisation, but that the union takes place in the act of solidification.

4. On mixing equal volumes of two solutions containing the proportions for the formation of a double salt, a very insignificant contraction occurs.

5. Since the solubility of double salts is often very different from that of their constituent salts, it would appear that these double salts have a real existence in solution.

6. The differences in the molecular volumes of salts of analogous elements and similar constitution are equal to the differences between their molecular weights.

7. The molecular volume of a substance in aqueous solution diminishes with increasing concentration of solution. In different solvents the molecular volumes of the dissolved substance are not identical, but always closely approximate. M. J. S.

Constitution of Salt Solutions inferred from their Behaviour to Carbonic Anhydride. By J. SETSCHENOFF (*Zeit. physikal. Chem.*, **4**, 117—125).—The aqueous solutions of salts of the strong acids absorb carbonic anhydride in accordance with Dalton's law under pressures of less than $\frac{1}{3}$ atm.; but the absorption coefficients of the salt solutions are smaller than those of water at the same temperatures, and invariably increase with dilution. The numerical law which this increase follows is expressed by the equation $y = \alpha e^{-\frac{k}{x}}$, y being the absorption coefficient of the salt solution, α that of water at the same temperature, x the volume of the solution, which varies with the dilution, and k a constant; this law, however, is an approximation, and not absolutely correct. The study of the behaviour of salt solutions towards carbonic anhydride also leads the author to the conclusion that a salt solution is a very weak chemical compound of the salt and water. The gas reacts simultaneously with the water and the distributed salt, and both reactions are to be regarded as of chemical nature. In its reaction with the water, the gas has to overcome the attraction of the latter for the salt, and the reaction with the salt may be regarded as an endeavour to displace a portion of the acid which is associated with the base. H. C.

Heat of Dissociation and Influence of Temperature on the Dissociation of Electrolytes. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **4**, 96—116).—The author measures the conductivities of various electrolytes in dilute solutions at 18° and 52°, and by means of the formula $\mu_{52} = \mu_{18} (1 + a_{35} \cdot 34)$ calculates the mean temperature coefficients, a_{35}, between those temperatures. The temperature coefficients of the more dissociated electrolytes are generally smaller the greater the conductivity. Hence the conductivities approach one another as the temperature rises. The change in the coefficients with the strength of the solution is not great as long as the latter remains small.

By means of the conductivity at two different temperatures, the heat of dissociation of an electrolyte can be calculated. This last is, per gram-molecule, $1{\cdot}945 \times 3{\cdot}35 \times T^2 d \log_{10} k/dt + 1{\cdot}945\ T$, and in order to calculate $d \log_{10} k/dt$, the values of k, the constant of dissociation, for two different temperatures must be known; these are obtained from the conductivities. A number of calculated values of the heats of dissociation of various electrolytes are given. It is noteworthy that the majority of these are negative quantities.

The heats of dissociation being known, it is possible to calculate also the heat of neutralisation, the assumption as to the mechanism of the process in dilute solution being similar to that made by Ostwald (this vol., p. 931). Thus, if of the acid, base, and resulting salt the fractions d_1, d_2, and d_3 are dissociated, and the corresponding heats of dissociation are W_1, W_2, and W_3, that of water being x, the heat of neutralisation of an acid by a base in dilute solution is given by—

$$- (1 - d_1)W_1 - (1 - d_2)W_2 + x + (1 - d_3)W_3.$$

The heats of neutralisation of a number of acids by sodium hydroxide are given as calculated by the above formula, and are in very fair agreement with the observed values.

From the dissociation theory, it can be shown that the conductivity at any temperature $\lambda_t = A_1 e^{-bt} (1 + \alpha t)$, where A_1 represents the amount of dissociation at the temperature t_0, b is constant, and α is the temperature coefficient. The function λ_t becomes a maximum when $(1 + \alpha t)b = \alpha$, so that above this temperature the conductivity decreases, that is, the temperature coefficient becomes negative. The maximum was calculated for hypophosphorous acid at 57°, and for phosphoric acid at 78°, and by direct observation it was found that the conductivity in the first case reaches a maximum at about 55°, and in the second case at 75°. The above is an additional confirmation of the truth of the dissociation theory. H. C.

Statical and Dynamical Methods of Measuring the Vapour Pressures of Chemically Combined and of Adsorbed Water.

By W. MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, **4**, 1—9).—Owing to the differences in the results obtained for the vapour pressures of some solid salts as measured by the statical and by his dynamical method, particularly in the case of Lescœur and Mathurin's observations on some of the alums, the author is led to a careful comparison of the two methods. He finds that both methods are in many respects equally trustworthy and accurate, but in the case of the statical method a difficulty arises, owing to the incomplete absorption of an excess of aqueous vapour by the solid salt, so that the pressure of decomposition cannot be exactly determined. In the case of potash alum, for instance, this is particularly noticeable, for, although the salt ceases to lose water when the relative pressure at 30° is above 0·085, the pressure must be raised to 0·26 before the salt will again take up water. The difference for other salts is not, however, quite as great as for this. H. C.

Diffusion of Acids and Bases into One Another. By J. STEFAN (*Monatsh.*, **10**, 201—219).—When very dilute ammonia is placed over a column of dilute hydrochloric acid, the surface of separation between the acid and the alkaline liquids remains well defined, as can be easily observed if the solutions are coloured with litmus, but the region occupied by the acid gradually extends upwards. In one experiment, a solution containing 1 gram-molecule of hydrochloric acid per litre was covered with a solution of ammonia containing one-sixteenth of a gram-molecule; the surface of separation rose 8·2, 16·5, and 24·5 mm. in one, four, and nine hours respectively, the rise being proportional to the square root of the time during which diffusion takes place. With the same hydrochloric acid, employing a solution of ammonia containing $\frac{1}{4}$ gram-mol., the surface of separation rose 5, 9·9, and 14·7 mm. in one, four, and nine hours respectively.

When a solution containing 1 gram-mol. of ammonia is employed, the region occupied by the acid extends upwards, rising 1·2, 2·3, and 3·5 mm. in one, four, and nine hours respectively, but when the ammonia is four times as concentrated, the surface of separation gradually sinks, and the depression is 1·2, 2·5, and 3·8 mm. in one, four, and nine hours respectively. If ammonia of a certain concentration were employed, the surface of separation would remain stationary. The concentration of the ammonia which would fulfil this condition would lie somewhere between that of the solutions employed in the last two experiments; the exact strength cannot be ascertained experimentally except with great difficulty, but it can be shown mathematically that the surface of separation would remain stationary if solutions of 1 mol. of hydrochloric acid and 1·8 mol. of ammonia respectively were employed.

The phenomena described above are determined by the relative concentrations of the acid and alkaline solutions; they are independent of their absolute values, at any rate as long as the latter are not very large.

Similar experiments were made with solutions containing 2 gram-mols. of hydrochloric acid and 0·5 gram-mol. of ammonia respectively. The region occupied by the acid extended 5, 9·9, and 14·8 mm. upwards in one, four, and nine hours' time.

When the hydrochloric acid solution contains only $\frac{1}{16}$ gram-mol., and the ammonia 1 mol., the surface of separation falls 3 9, 8·2, and 11·9 mm. in one, four, and nine hours respectively; with solutions containing 1·5 gram-mol. of hydrochloric acid and 12 gram-mols. of ammonia respectively, the surface of separation falls 3·9, 8·4, and 11·6 mm. in the same times. In those experiments in which the region occupied by the ammoniacal liquid extends downwards, the two solutions do not remain so sharply separated, and the surface of separation is often irregular.

In one experiment with solutions containing 1 gram-mol. of soda and $\frac{1}{16}$ gram-mol. of acetic acid respectively, the region occupied by the alkaline liquid extended 5·8, 11·6, and 17·4 mm. upwards in one, four, and nine hours, and 28·5, 40·5, and 49·7 mm. in one, two, and three days respectively.

The apparatus employed in these experiments consists of two graduated glass tubes (120 mm. in length, 7 mm. in internal and 23 mm. in external diameter), fixed, with their open ends turned towards each other, on a perpendicular brass stand, so that they can be moved up and down or rotated round the stand. The open ends have ground edges, the other extremities being closed with glass plates, fastened on with cement. The underneath tube is filled *in situ;* the other is filled, then inverted, and any liquid which falls out replaced with a small pipette. At the commencement of the experiment the open ends of the two tubes are brought to the same level, and they are then rotated until the one is exactly over the other.

The author discusses the phenomena of diffusion mathematically, and, from the data given above, the coefficient of diffusion of ammonia is found to be 0·92, and that of hydrochloric acid 3·02.

From observations made in a similar manner with ammonia and various acids, the diffusion coefficients are found to be as follows:—Nitric acid, 2·93; sulphuric acid, 1·82; oxalic acid, 1·14; and acetic acid, 0·88. In all the experiments, solutions containing one equivalent of the acid and one-sixteenth of an equivalent of ammonia respectively were employed. In two experiments in which solutions of one equivalent of base and one-sixteenth of an equivalent of acetic acid were employed, the diffusion coefficient of potash was found to be 0·73, and that of soda 1·57. The above values are for the temperature of 21°.

The diffusion coefficients of hydrochloric acid, nitric acid, and sulphuric acid are considerably larger than those found by Scheffer (*Zeit. physikal. Chem.*, **2**, 390—404) by the ordinary methods, but the results are not comparable, as Scheffer experimented at lower temperatures; the coefficients found for the other substances agree better, and in some cases very well. The diffusion coefficients found for the three acids named above, and those of potash and soda, are in the same ratio as the molecular conductivities of these electrolytes as determined by Kohlrausch; but the coefficients of oxalic acid, acetic acid, and ammonia are larger than they should be if they followed the same rule. The diffusion coefficients, and those values which are termed the coefficients of chemical affinity, also stand in a direct relation to one another. F. S. K.

Molecular Volumes of Aromatic Compounds. By S. FEITLER (*Zeit. physikal. Chem.*, **4**, 66—88).—The compounds examined were chloro-, bromo-, and iodo-benzene, and the chloro- and bromo-toluenes. In each case the volume was determined as a function of the pressure, that is, vapour-tension of the liquid, this being preferred to referring both quantities to the same temperature, as differences in pressure are more easily measured than those in temperature. Great care was expended in the preparation of perfectly pure material, the method of preparation and purification of each compound being given in detail in the paper.

Putting the results in curve form, with volumes as ordinates and pressures as abscissæ, the similarity of the curves with those obtained by Neubeck (Abstr., 1888, 895) is at once noticeable. The curve for bromobenzene lies nearer that for chlorobenzene than that for iodobenzene. Of the three isomeric chloro- and bromo-toluenes, the ortho-compound has always the smallest, and the para-compound the greatest, molecular volume. That of the meta-compound lies between, but nearer to that of the para- than to that of the ortho-compound. This relation holds for all pressures, and agrees with that found by Neubeck for other toluene-derivatives.

If, in a series of similar constituted compounds, the molecular volume of the original be subtracted from that of the substituted compound, the molecular volume of the substituent less that of hydrogen is obtained. For one and the same substituent, the numbers thus found differ considerably in different compounds. Taking the volumes occupied by the different groups, less hydrogen, in the benzene-derivatives as the standard, then the substitution of an amido-, chloro-, methyl-, bromo-, or nitro-group in toluene in the ortho-position brings about a mean decrease in the volume of the group less that of hydrogen of 2·4 units. In the meta-position, the influence of the methyl-group on the volume of the substituent is already much smaller, and in the para-position is scarcely appreciable.

H. C.

Gas Generator with Continuous Removal of the Exhausted Solution. By T. Breyer (*Zeit. anal. Chem.*, 28, 438—440).—The solid from which the gas is prepared is contained in a wide cylinder drawn out below to a moderately narrow tube. This tube passes through a cork in a small, wide-mouthed bottle, whilst a second tube passing through the same cork is connected by rubber tubing to a hook-shaped glass tube hanging over the lip of a flask which can be placed at any elevation. The decomposing liquid is supplied from a higher reservoir by means of a stopcock tube passing through the cork in the top of the wide cylinder, through which also the gas delivery tube passes. To use the apparatus, the wide-mouthed bottle is filled with water, and the flask is raised as far as possible. The acid is then allowed to drop in. The pressure of the gas forces the water up in the rubber tube. When the gas begins to bubble through the wash bottle and the liquid on which it is to act, the flask is lowered until the water just begins to overflow into it. As the exhausted acid rises in the generating cylinder, its pressure drives over more water into the flask, and its level is thus maintained constant.

M. J. S.

Inorganic Chemistry.

Hydrated Metallic Chlorides. By P. SABATIER (*Bull. Soc. Chim.* [3], **1**, 88—90).—The following crystalline chlorides have been prepared:—

$CuCl_2,2H_2O$; $MnCl_2,4H_2O$; $FeCl_2,4H_2O$; $Fe_2Cl_6,12H_2O$;
$Al_2Cl_6,12H_2O$; $CaCl_2,6H_2O$; $SrCl_2,6H_2O$; $MgCl_2,6H_2O$;
$CoCl_2,6H_2O$; $NiCl_2,6H_2O$;

and when placed in a vacuum for three months at 20° over sulphuric acid respectively yielded:—

$CuCl_2$; $3MnCl_2,5H_2O$; $FeCl_2.2H_2O$; $Fe_2Cl_6,5H_2O$;
$Al_2Cl_6,12H_2O$ (not altered); $CaCl_2,H_2O$; $SrCl_2,2H_2O$;
$MgCl_2,5H_2O$; $CoCl_2,2H_2O$; $NiCl_2,2H_2O$.

When ferrous, nickelous, manganous, strontium, and magnesium chlorides are crystallised from hydrochloric acid, the crystals obtained have the formulæ last given. T. G. N.

Basic Zinc-ammonium Carbonate. By G. KASSNER (*Arch. Pharm.* [3], **27**, 673—678).—A feeble electric current was passed through an ammonium carbonate solution, the positive pole (anode) being a zinc rod. After some time, transparent, needle-shaped crystals appeared on the surface of the liquid, and later a white powder was deposited in the vessel. The compound was insoluble in water; potassium hydroxide caused a copious evolution of ammonia, and acids disengaged much carbonic anhydride. There was no change on heating it at 150°, but at a higher temperature water was expelled and also ammonia. Analysis gave ZnO 66·01, NH_3 4·26, CO_2 21·07, H_2O 8·28, total 99·62; which approximates to the formula $3ZnO,NH_4{\cdot}OH,2CO_2 + H_2O$. Further consideration leads to the view that the substance is a basic zinc carbonate in which the hydrogen of a basic group ($-ZnOH$) is displaced by ammonium. J. T.

Halogen-mercuric Acids. By G. NEUMANN (*Monatsh.*, **10**, 236—241).—The halogen-mercuric acids are obtained in a crystalline condition when the halogen acid is saturated with the corresponding halogen-mercury salt and the solution kept at a low temperature over sulphuric acid and calcium oxide. The saturated solutions are most quickly prepared by gently warming excess of the mercury salt with the halogen acid and filtering the cold solution through asbestos. The crystalline compounds obtained at temperatures varying from 0° to −4° gave on analysis results corresponding with the general formula $HHgX_3$ where $X =$ halogen. In one experiment, when the temperature fell to −12° crystals of a chloro- and a bromo-derivative were obtained, the analysis of which showed that they had the general formula H_2HgX_4; in crystalline form and in their other properties, however, they resembled the compounds of the formula $HHgX_3$.

The halogen-mercuric acids are very readily decomposed by moisture and by heat, so that, as they cannot be analysed in the usual way, the proportion of mercury to halogen only was determined.

They probably contain water of crystallisation, as, even when dried for a long time in the air, they still retain moisture. On heating, the crystals melt partially; the water of crystallisation probably serving as a solvent for some of the salt. When dry hydrogen chloride is passed for 1½ hours over mercuric chloride cooled in a mixture of snow and salt, the increase in weight is only 0·0021 gram, a fact which is further evidence in support of this view.

Chloro-mercuric acid, $HHgCl_3$, crystallises in long, transparent needles (compare Davy, *Kraut-Gmelin,* 1875, **3**, 797).

Bromo-mercuric acid, $HHgBr_3$, resembles the preceding compound in appearance (compare Löwig, *ibid.*, 1875, **3**, 781).

Iodo-mercuric acid, $HHgI_3$, crystallises in yellow needles (compare Boullay, *Ann. Chim. Phys.*, **34**, 340). F. S. K.

Mercury Oxychlorides. By K. THÜMMEL (*Arch. Pharm.* [3], **27**, 589—605).—Roucher (*J. pr. Chem.*, **49**, 1850, 377) indicates 15 oxychlorides, but only five of these can be considered as definite compounds, namely:—the oxydichloride, $HgO,2HgCl_2$; monoxychloride, $HgO,HgCl_2$; dioxychloride, $2HgO,HgCl_2$; trioxychloride, $3HgO,HgCl_2$; and tetroxychloride, $4HgO,HgCl_2$. All others are either modifications or mixtures of these oxychlorides. The oxydichloride is produced in all mercuric chloride solutions when these are treated with oxide, but its ready decomposition hinders its separation from these solutions. It can be obtained by heating on the water-bath a mixture of 1 part of yellow or red oxide and 10 parts of chloride with 60 parts water, and stirring until no more of the light yellow powder consisting of the oxychloride separates; this is washed and dried, and then washed with ether free from alcohol and water, to remove any residual chloride. It forms a fine, pale-yellow powder which under the microscope appears as small, colourless, polyhedral crystals. Cold alcohol and warm water decompose it with separation of the dioxychloride. Sodium hydroxide solution separates red oxide. The monoxychloride has not yet been isolated; it is, however, present in all solutions of the alkali hydrogen carbonates which contain mercuric chloride. As the monoxychloride is less soluble in water than the chloride, precipitates appear as soon as the solution contains less than 20 mols. of hydrogen sodium carbonate or 45 mols. hydrogen potassium carbonate to 1 mol. of mercuric chloride. The monoxychloride, however, does not come down as such, but as trioxychloride. The dioxychloride is known in two modifications. The *red* variety appears when 2 mols. of hydrogen sodium carbonate and 1 mol. of mercuric chloride are brought together in solution. The red precipitate appears under the microscope as ruby-red, four-sided plates. Alkaline carbonates or chlorides convert it into tetroxychloride. On heating the dry powder, it is converted into the polymeric black dioxychloride. This *black* variety is produced by adding mercuric oxide to a hot mercuric chloride solution, or on mixing equivalents of red oxide and of chloride solution in the cold; also when the trioxychloride is treated with mercuric chloride solution in the cold. Trioxychloride is decomposed by heat into black dioxychloride and brown tetroxychloride. The black compound, which appears as black rhombic plates under the microscope, yields a dark reddish-brown powder. Alkaline carbonates and chlorides do not decompose it; sodium hydroxide separates red oxide, whilst the red dioxychloride gives yellow oxide under the same conditions. The trioxychloride appears as a yellow precipitate when an alkaline carbonate or hydrogen carbonate is added to mercuric chloride solution; but excess of alkali or of chloride readily converts it into brown tetroxychloride or red dioxychloride. The pure trioxychloride may be prepared by treating freshly precipitated yellow oxide or washed red oxide with mercuric chloride solution. In the first case the product is light yellow, and with potassium hydroxide gives yellow oxide; in the second case it is reddish-yellow, and gives the red oxide with potash. Under the microscope, the pale yellow compound appears as pale yellow needles, the red compound as truncated prisms. The substance becomes dark brown when powdered, and black when heated to a temperature below 100°. It is decomposed into di- and tetra-oxychloride when warmed with water. Exposure to light blackens it, and the crystalline substance (reddish or light yellow) is converted into dioxychloride by treatment with mercuric chloride. Millon (*Arch. Pharm.*, **23**, 962) has obtained a red modification of trioxychloride, which is also easily decomposed. The tetroxychloride appears either as a brown, amorphous powder, or crystallises in brown, reddish-brown to bronze, six-sided plates. The amorphous variety is obtained by precipitating mercuric chloride solution with hydrogen potassium carbonate ($HgCl_2$; 30 to 35 $KHCO_3$), or by the addition of normal carbonate to a boiling chloride solution. The crystallised variety is produced by precipitating the chloride in the cold with hydrogen alkali carbonate, by heating concentrated alkali monoxychloride solutions, or by agitating aqueous chloride solution with red oxide (1 : 6). Both amorphous and crystalline varieties give the yellow oxide on treatment with potash lye. All the oxychlorides when heated give sublimates containing both mercuric and mercurous chlorides. Alcohol and ether in the cold, and water on warming, extract chlorides containing oxygen. J. T.

Specific Gravity and Composition of Tin-Lead Alloys. By O. Kleinstück (*Arch. Pharm.* [3], **27**, 628—640).—The conclusion arrived at is that the sp. gr. of tin alloys, as calculated from their composition, on the supposition that no volume change results from alloying, does not widely vary from the sp. gr. determined experimentally. J. T.

A New Tin Oxide. By W. Spring (*Bull. Soc. Chim.* [3], **1**, 180—182).—Hydrated barium dioxide is added in excess to a hydrochloric acid solution of stannous chloride, and the turbid liquid thus produced is dialysed until barium chloride no longer passes through the membrane. The colloïd residue, after evaporation on the water-bath, yields a white mass whose formula, determined by direct estimation of both water and oxygen, is $H_2Sn_2O_7$; it may be regarded as the derivative of a perstannic anhydride, SnO_3, resulting from the following reactions:—

$$SnCl_2 + BaO_2 = SnOCl_2 + BaO;$$
$$SnOCl_2 + BaO_2 = SnO_3 + BaCl_2.$$

The author proposes to continue this research. T. G. N.

Behaviour of Metastannic Acid to Bismuth and Iron Oxides. By C. LEPÉZ and L. STORCH (*Monatsh.*, **10**, 283—294).—In the estimation of tin in alloys, oxidation to metastannic acid is the most convenient method, but Rose has shown (*Ann. Phys. Chem.*, **112**, 164) that when other feebly basic metals are present the metastannic acid formed contains considerable quantities of such metals. Rose states that when bismuth is present, the ignited residue contains the oxide of that metal, and is of a reddish-yellow colour. The authors have carefully repeated Rose's work and find that the metastannic precipitate sometimes contains as much as 12 per cent. of bismuth which cannot be washed out, but the residues obtained were always yellowish-white in colour and not reddish-yellow. It is pretty certain that the bismuth is mainly present as bismuth stannate.

Rose also states that when iron is present in small quantities the metastannic acid precipitated contains iron, but that when any considerable quantity of iron is present both the tin and iron remain in solution. Experimenting on this point, the authors found that when tin was digested with a solution of iron in excess of nitric acid, it was dissolved to the extent of 2 and even 3 atoms of tin to 1 atom of iron, forming yellow solutions. Solutions containing more than 2 atoms of tin were unstable, but solutions containing 2 atoms or less of tin to 1 of iron could be boiled and even evaporated to dryness in a vacuum. In these solutions, concentrated nitric acid produced a yellowish-precipitate, which, however, redissolved on dilution. Strong hydrochloric acid caused a similar precipitate which dissolved in excess of the precipitant. Sulphuric acid and alkaline sulphates cause a permanent precipitate. Alkaline nitrates and chlorides, acetic acid, and ammonium tartrate are without action, but free tartaric acid causes a precipitate on warming. Potassium permanganate is not decolorised by the solution, but the solution itself is decolorised by stannous chloride. From different solutions, the authors have obtained by evaporation in a vacuum three different compounds giving numbers corresponding with the formulæ $1{\cdot}8(SnO_2,H_2O) + Fe_2O_3,1{\cdot}8N_2O_5$; $4(SnO_2,H_2O) + Fe_2O_3,1{\cdot}1N_2O_5$; and $6(SnO_2.H_2O) + Fe_2O_3,1{\cdot}6N_2O_5$. The reactions of these solutions show that the iron is present in the ferric state, but do not decide whether the tin is in the form of metastannic acid or whether, as the authors believe probable, in the form of a soluble orthostannic acid. The nitric acid evidently forms an essential part of the compounds. When a mixture of stannic and ferric hydrates is precipitated from the mixed nitrates by a slight excess of ammonia and the precipitate washed free from ammonium chloride, the precipitate (still retaining a trace of free ammonia) dissolves in water to a clear solution. If the last trace of ammonia is removed by dialysis the solution gelatinises, but the addition of a trace of ammonia again causes complete solution. Any salts added to these solutions cause immediate precipitation.

On mixing solutions of soluble ferric hydrate and soluble stannic hydrate, immediate precipitation of both metallic oxides takes place.

Chromic nitrate is similar in its action to ferric nitrate; ceric nitrate dissolves, at most, traces of tin; aluminium, uranium, cobalt, nickel, and copper nitrates do not dissolve metastannic acid. When tin is strongly heated with ferric sulphate and excess of strong sulphuric acid until a part of the acid is volatilised, the whole allowed to cool, and then treated with cold water, a considerable quantity of tin goes into solution. When this solution is heated, the tin is precipitated. If tin, however, is digested with an acid solution of ferric sulphate either at 100° or at the ordinary temperature, no tin is dissolved.

When the acid ferri-stannic solutions are treated with hydrogen sulphide in the cold, no precipitation takes place for some time, and then only one of sulphur, and it is necessary to heat the solution to cause precipitation of stannic sulphide, which then contains iron. The separation of the iron and tin is, however, at once effected by ammonium sulphide in presence of ammonium chloride.

L. T. T.

Stannic Sulphide and Thiostannic Acid. By L. Storch (*Monatsh.*, 10, 255—282).—The author noticed that if ammonium oxalate is added to a solution of stannic chloride, the precipitate produced by hydrogen sulphide is reddish-brown. When aqueous hydrogen sulphide is used as the precipitant, the solution first becomes intensely yellow to yellowish-red, and from this the reddish-brown precipitate gradually separates. Other oxalates give the same result. Experiments were then made to test whether this property was a peculiarity of oxalic acid or common to other acids. For this purpose, various acids were added to a solution of sodium thiostannate, prepared by saturating a solution of sodium stannate with hydrogen sulphide. Hydrochloric, sulphuric, and dichloracetic acids caused an immediate precipitation of yellow stannic sulphide, but oxalic, phosphoric, monochloracetic, tartaric, citric, succinic, and acetic acids produced brownish-yellow solutions, from which reddish-brown precipitates separated more or less slowly. These results showed that this reaction was dependent on the affinity (avidity) of the acid, those causing precipitation having affinities ranging, according to Ostwald, from 25—100 (HCl = 100), the avidities of those which did not determine precipitation of the yellow sulphide being below 20.

The brown precipitates contained only slightly more sulphur than corresponded with the formula SnS_2, and did not appear to be homogeneous. Attempts to isolate the compound formed proved unavailing. When a dilute solution of oxalic acid is added to a solution of sodium thiostannate in quantity only just sufficient to neutralise the sodium, a deep yellow solution is produced which gradually changes to reddish-brown, but remains clear for hours, and may be partially concentrated before separation of the reddish-brown precipitate occurs. Acetic and oxalic acids produce no immediate precipitates from this solution. Ammonia and potash gradually decolorise it, as do sodium and ammonium carbonates, ammonium chloride, and sodium acetate, although more slowly. Many salts and strong acids cause precipitation. As the substance formed could not be isolated, the author estimated the ratio of sulphur to tin in this solution after the free hydrogen sulphide had been removed by a current of air. The result showed the presence of 3 atoms of sulphur to one of tin. The author therefore concludes that *thiostannic acid*, H_2SnS_3, is present in this solution. It is also probably present in small quantities in the brown precipitate.

Kuhn (*Annalen*, **89**, 114) describes the formation of thiostannic acid as an olive-brown precipitate when a concentrated solution of sodium thiostannate is decomposed by hydrochloric or acetic acid. The author has repeated these experiments and obtained brown precipitates, but these never contained more sulphur than that required by the ratio Sn : S = 1 : 2·19, and therefore they were not the pure thio-acid, but mixtures of it with the sulphide. L. T. T.

Mineralogical Chemistry.

Rock from Colorado, containing Sodium-amphibole, Astrophyllite, Pyrochlorite, and Zircon. By A. Lacroix (*Compt. rend.*, **109**, 39—41).—This rock occurs in veins in the granite of the region round about San Peter's Dome, Cheyenne Cañon, and El Paso, in Colorado. Sometimes it is very coarsely crystalline like pegmatite; sometimes it is finely crystalline. The constituent minerals are sodium-amphibole or riebeckite, astrophyllite, pyrochlorite, fluorite, zircon, biotite, microcline, albite, anorthite, and quartz. The rock very closely resembles the granite in the Island of Socotra, and a rock found by Le Verrier in Corsica. The amphibole in the Colorado rock, the riebeckite of Socotra, and the arfvedsonite of Greenland differ mainly in the relation between the ferrous and ferric oxides, and are identical in optical properties. The optical properties of the astrophyllite, which sometimes occurs in crystals 15 cm. long, are identical with those of the astrophyllite of Langesundfjord. Zircon is very abundant, the crystals reaching 1 cm. in length, and is accompanied by cubic crystals which seem to consist of pyrochlorite. Albite is abundant and forms small lamellæ flattened along (010), but the microcline has to a considerable extent undergone alteration. Quartz is distributed throughout the rock, sometimes in small granules, sometimes in large platy masses. C. H. B.

Mineral Water of the Ottili Spring, Suhl, Thuringia. By E. Reichardt (*Arch. Pharm.* [3], **27**, 645—649).—The water of an older spring in the same locality was described by the author in 1878 (*Arch. Pharm.*, **214**, 252). The temperature of the new spring is 13·1°, of the old one 12·5°; the reaction is neutral. Sp. gr. at 9° = 1·0095, another sample later at 25° = 1·0075; old spring at 20° = 1·0074. Total solids dried at 100° 14·14, 14·26 grams per litre.

The analysis of the old spring water is here given for the purpose of comparison, the results being expressed in grams per litre:—

	New spring.	Old spring.
Chlorine	6·8496	4·7720
Bromine	0·0369	0·0051
Iodine	0·00021	trace
Sulphuric anhydride	0·2918	0·2027
Calcium oxide	2·4360	1·5749
Magnesium oxide	0·0078	0·0681
Barium oxide	0·00012	0·0016
Strontium oxide	0·00016	0·0013
Iron oxide	0·00019	0·0003
Manganous oxide	0·00009	0·0005
Aluminium oxide	0·0	0·0
Sodium	2·5507	1·6449
Potassium	0·0863	0·3130
Rubidium	trace	trace
Cæsium	,,	,,
Lithium	0·0044	0·0027
Silicic anhydride	0·0117	0·0125
Organic matter	0·0340	0·0500
Carbonic anhydride	0·0414	0·0844

Free carbonic anhydride at 13·1° and 760 mm. = 5·78 c.c.

J. T.

Organic Chemistry.

Manufacture of Iodoform. By H. SUILLIOT and H. RAYNAUD (*Bull. Soc. Chim.* [3], 1, 3—4).—When a slight excess of a dilute solution of sodium hypochlorite is added to potassium iodide (50 parts), acetone (6 parts), and sodium hydroxide (2 parts), previously dissolved in cold water (1 or 2 litres), iodoform is precipitated in almost theoretical amount, according to the equations:—

$$KI + NaClO = KIO + NaCl;$$
$$CH_3{\cdot}CO{\cdot}CH_3 + 3KIO = CHI_3 + CH_3{\cdot}COOK + 2KHO.$$

The presence of considerable quantities of neutral alkaline salts does not affect the reaction, and the process can be applied to kelp lyes from which the sulphides and sulphites have been removed.

T. G. N.

Reduction of Copper Salts by Sugars. By MONNET (*Bull. Soc. Chim.* [3], 1, 83—85).—A saturated solution of saccharose precipitates crystals of metallic copper from copper sulphate, inversion preceding. After some time, the whole of the copper is thrown down.

Lactose and dextrose react similarly but more slowly; reduction occurs at all temperatures, but is favoured by heating.

Cupropotassic solution is reduced by a concentrated saccharose solution to cuprous oxide, and after prolonged boiling to amorphous metallic copper; in the case of lactose and dextrose, a short ebullition determines complete reduction to the metallic state. T. G. N.

Chlorination of Ethyl Acetoacetate. By I. Ossipoff (*Bull. Soc. Chim.* [3], 1, 165—166).—The author wishes to reserve to himself the research which he has begun on the influence of temperature on the chlorination of ethyl acetoacetate. Up to the present his results are as follows:—

At 18—20°, a monochlorinated-derivative, boiling at 192—198° and containing 20·18 Cl per cent., is alone obtained.

At 50°, three chlorinated-derivatives are produced:—

(1.) Boiling at 208—212° containing 34·16 Cl per cent.
(2.) Boiling at 214—217° „ 37·11 „ „
(3.) Boiling at 217—230° „ 53·31 „ „

At 100°, a single chlorinated-derivative is formed, boiling at 208—212°. T. G. N.

Electrolysis of Solutions of Organic Potassium Salts and of Molten Potassium Acetate. By Lassar Cohn (*Annalen*, **251**, 335—359).—Concentrated solutions of various potassium salts were exposed to the action of a galvanic current of four or eight small zinc-platinum elements. The solutions were placed in a beaker containing a small porous cell; one electrode dipped into the solution in the cell, and the second electrode was immersed in the solution surrounding the cell. *Potassium bromacetate* is reduced to acetic acid; carbonic anhydride is liberated at the positive pole, and when the solution becomes acid bromine is liberated. No hydrogen escapes at the negative pole until the greater part of the bromacetic acid is reduced to acetic acid. *Potassium chloracetate* yields analogous results. *α-Bromopropionic acid* yields a small quantity of hydrogen, carbonic anhydride, bromine, and a small quantity of hydrocarbon bromine-derivatives. *Dibromacetic acid* gives off hydrogen at the negative pole, and carbonic anhydride and bromine at the positive. Bromosuccinic acid is reduced to succinic acid, whilst carbonic anhydride mixed with carbonic oxide is set free at the positive pole. When the solution surrounding the positive electrode becomes acid, pure carbonic anhydride and bromine are liberated; after a time, oxygen is also evolved. A small quantity of fumaric acid is formed during the operation.

Dibromosuccinic acid is successively reduced to bromosuccinic acid and succinic acid; carbonic anhydride is set free, but no bromine is liberated. *Isodibromosuccinic acid* yields succinic acid, carbonic anhydride, and bromine. Bromofumaric acid yields succinic acid and carbonic anhydride, but no bromine.

Isosuccinic acid is most conveniently prepared by acting on potassium α-bromopropionate with potassium cyanide, the product being converted into potassium isosuccinate by boiling with potassium hydroxide. On electrolysis, potassium isosuccinate evolves hydrogen, carbonic anhydride, and oxygen. *Bromisosuccinic acid* crystallises in transparent plates, and melts with decomposition at 130°. The acid begins to decompose at 95°. The *barium salt*, $BaC_4H_3BrO_4 + 2H_2O$, crystallises in needles. The potassium salt is decomposed by electrolysis, yielding isosuccinic acid, carbonic anhydride, and bromine. *Dibromisosuccinic acid* melts at 101°, and is soluble in alcohol, ether, and water, but the aqueous solution is decomposed by boiling. The potassium salt is deliquescent: the barium salt contains 2 mols. H_2O, and crystallises in needles. The acid is decomposed by electrolysis into isosuccinic acid, hydrogen, bromine, and carbonic anhydride. The potassium salts of benzoic, phthalic, and the hydroxybenzoic acids are decomposed by electrolysis, yielding hydrogen at the negative, and carbonic oxide, oxygen, carbonic anhydride, and phthalic, benzoic, or the hydrobenzoic acids at the positive pole. Molten potassium acetate, on electrolysis, yields carbon and equal volumes of hydrogen and marsh gas at the negative pole, and pure carbonic anhydride at the positive. W. C. W.

Geometrical Constitution of the Crotonic Acids and of their Halogen Substitution-products. By A. MICHAEL (*J. pr. Chem.* [2], **40**, 29—44).—A reply by the author to the counter-criticisms of J. Wislicenus published in a paper of the above title in *Annalen*, **248** (this vol., p. 236; see also Abstr., 1888, 1147 and 1176).

A. G. B.

Action of Hydriodic Acid on the Crotonic Acids. By A. MICHAEL and P. FREER (*J. pr. Chem.* [2], **40**, 95—96).—According to Hemilian, hydriodic acid acts on solid crotonic acid to form much solid α-iodobutyric acid and a little fluid β-iodobutyric acid, a result contrary to the rule that the halogen unites with the relatively most positive of the unsaturated carbon-atoms of crotonic acid.

The authors have treated solid crotonic acid with strong and weak hydriodic acid, both hot and cold, but have obtained in each case well crystallised β-iodobutyric acid of low melting point as the only product. When β-iodobutyric acid is heated with an excess of soda solution, it yields solid crotonic acid.

Fluid allocrotonic acid, which can be obtained perfectly pure by distillation out of contact with air, gives the same β-iodobutyric acid, and not a fluid acid as stated by Fittig and Alberti. A. G. B.

Composition of Solid Animal and Vegetable Fats. By R. BENEDIKT and K. HAZURA (*Monatsh.*, **10**, 353—356).—Hazura and others have shown that all vegetable oils seem to contain linoleic acid. The authors have now examined palm-oil and also cacao-butter, and find linoleic acid in both, whilst oleic acid alone could be obtained from the numerous solid and liquid fats and oils of animal origin which they and others have previously examined. Lard and tallow also gave the same result. The authors believe this will enable the analyst to decide whether commercial oleic acid or "elaïn"

—the liquid acid obtained in soap making—is of vegetable or animal origin. If of vegetable origin, it will yield sativic acid on oxidation by potassium permanganate, if of animal origin, dihydroxystearic acid will be formed. L. T. T.

Non-drying Oils. By K. Hazura and A. Grüssner (*Monatsh.*, **10**, 242—249).—Earth-nut oil was saponified with alcoholic potash, the solution poured into a large quantity of cold water, neutralised with acetic acid, and treated with lead acetate; the precipitated lead salts were pressed and extracted first with cold (A), then with warm (B) ether, and the acids precipitated from the extracts separately with dilute sulphuric acid.

The mixture of acids (60 grams) obtained from the cold ethereal extract A was oxidised with potassium permanganate, the filtered solution acidified with dilute sulphuric acid, and the dry precipitate extracted with ether. The insoluble residue (A_1, 45 grams) consisted of dihydroxystearic acid and sativic acid (7 grams), which were separated by extracting the mixture with boiling water, and the portion soluble in ether, A_2, was treated as described below.

The mixture of acids (70 grams) obtained from the hot ethereal extract B was oxidised with potassium permanganate, the acid precipitated from the filtrate and treated with ether; the residue (B_1, 45 grams) yielded the same products as A_1, namely, sativic acid and dihydroxystearic acid.

The portion soluble in ether (B_2, 14 grams) was mixed with the solution A_2, obtained as described above, and the acids fractionally crystallised from alcohol. The first three fractions were washed with ether and recrystallised from alcohol; the product, which melted at 122—124°, was much more readily soluble in ether and alcohol than dihydroxystearic acid, and probably consisted principally of dihydroxypalmitic acid (m. p. 116°). The analysis gave results agreeing with those required by a mixture of dihydroxypalmitic acid and dihydroxystearic acid, so that the oxidation-products of the acids present in A_2 and B_2 consist probably of the two acids just named.

An acid melting at 45°, which probably consisted principally of hypogæic acid, was isolated from earth-nut oil by Gössmann and Scheven's method (*Annalen*, **94**, 230), but it seems that this acid can be isolated by their method only when a large quantity is present in the sample.

The above experiments show that, on oxidation, the unsaturated fatty acids of earth-nut oil yield sativic acid, dihydroxystearic acid, and dihydroxypalmitic acid, so that the unsaturated acids contained in the oil itself are linoleic acid and oleic acid, and probably hypogæic acid. Earth-nut oil from different sources contains variable quantities of hypogæic acid.

The liquid fatty acids of oil of almonds and of oil of sesame were oxidised separately with potassium permanganate, and the crude products investigated as described in the case of olive oil. Sativic acid and dihydroxystearic acid were obtained in both cases, showing that the two oils contain the glyceride of linoleic acid as well as that of oleic acid. The quantity of linoleic glyceride is considerable in both oils.

Analyses of the fatty acids of olive oil by Oudemann's method showed that olive oil contains 13 per cent. of glycerides of saturated fatty acids, and 87 per cent. of glycerides of unsaturated fatty acids.

F. S. K.

Oily Acids from Lycopodium. By A. Langer (*Arch. Pharm.* [3], **27**, 625—628; compare Abstr., 1889, 741).—Bukowski (*Chem. Ztg.*, 1889, No. 21, 174) investigated the oil taken from fresh spores, and found that it had a neutral reaction and contained the following:—Phytosterin, $C_{25}H_{42}O$, 0·3 per cent.; lycopodic acid, $C_{18}H_{36}O_4$, 2·0 per cent.; oleic acid, $C_{18}H_{34}O_2$, 80·0 per cent.; arachidic acid, $C_{20}H_{40}O_2$, stearic acid, $C_{18}H_{36}O_3$, and palmitic acid, 3·0 per cent.; glycerol, 8·2 per cent.; loss, 6·5 per cent. The author contends that the oleic acid, which is the chief constituent, has the composition $C_{16}H_{30}O_2$, as given in his previous paper, and as deduced from fusions with alkali and oxidation with potassium permanganate. J. T.

Action of Zinc-ethyl on Succinic Chloride; of Zinc-ethyl and Zinc-methyl on Phthalic Chloride; Pyrotartaric Chloride. By Rjasantzeff (*Bull. Soc. Chim.* [3], **1**, 166—167).—Zinc ethide reacts with succinic chloride to form a compound which does not decompose on distillation, and when warmed with baryta-water yields a salt corresponding with a hydroxy-acid.

When the product of the reaction between zinc ethide and phthalic chloride at 40—55° is decomposed by water, crystals of a compound, $C_{12}H_{14}O_2$, are obtained melting at 54° and boiling at 250°.

Zinc methide and phthalic chloride yield a substance, $C_{10}H_{10}O_2$, crystallising in scales which melts at 68° and boils at 240°; it is soluble in alcohol and ether, and is oxidised to benzoic acid by fusion with potassium hydroxide. Both these compounds can be distilled in a current of steam.

Pyrotartaric chloride, prepared from methylsuccinic acid, is a yellowish, mobile liquid boiling at 190—193°, and but slowly decomposed by water. T. G. N.

Aldehydic Condensation-products of Carbamide, and Detection of Carbamide. By E. Lüdy (*Monatsh.*, **10**, 295—316).—The methods hitherto used for the detection of small quantities of carbamide being very unsatisfactory, the author has examined some of the condensation-products of carbamide with aldehydes in the hopes of finding a satisfactory reaction.

Methylenecarbamide is too uncertain in its formation and requires concentrated solutions of carbamide. The acraldehyde-derivative is a white, porcelain-like substance having the formula $2CH_4N_2O,3C_3H_4O$; Schiff also obtained a similar compound (*Annalen*, **151**, 186). It turns yellow at 225°, and chars at 250° without previous fusion. It is rendered soft by boiling water and dissolves slightly, but is insoluble in alcohol and ether. Its formation is, however, somewhat uncertain, and it is therefore unsuited as a test for carbamide. The benzaldehyde-derivative of carbamide is soluble in alcohol and therefore only formed from strong solutions.

The author finds the best test for carbamide to be the formation of nitrobenzodiureïd, $NO_2\cdot C_6H_4\cdot CH(NH\cdot CO\cdot NH_2)_2 + H_2O$, described by Schiff (*loc. cit.*). This is obtained when orthonitrobenzaldehyde in slight excess is added to even a very dilute alcoholic solution of carbamide, and the whole warmed gently. It melts at 200°, but when present in small quantities it is most conveniently detected by resolving it into its constituents by boiling it with slightly acidified water, and proving the presence of nitrobenzaldehyde by the red coloration produced by phenylhydrazine. The test is best carried out as follows; a slight excess of nitrobenzaldehyde is added to the alcoholic solution supposed to contain carbamide, the mixture is heated for some time on the water-bath and allowed to cool. If carbamide is present, a white precipitate is formed. Most of the excess of nitrobenzaldehyde volatilises during the heating on the water-bath. Any trace still remaining is removed by once washing with alcohol. Water slightly acidified with sulphuric acid is then added to the residue, and the whole boiled; if in the resulting solution a few drops of a solution of phenylhydrazine produces a red colour, this shows the presence of nitrobenzaldehyde and consequently of carbamide. As the condensation-product is very slightly soluble in alcohol, it is best, if no residual product is obtained, to divide the alcoholic solution into two parts; to one add phenylhydrazine at once, to the other add a drop or two of dilute sulphuric acid, boil, and then add phenylhydrazine. If any carbamide-derivative be present, the latter half will show a stronger red coloration than the former.

When a few drops of strong sulphuric acid is added to the alcoholic mixture of carbamide and orthonitrobenzaldehyde, a different condensation-product is obtained. This has the formula $C_{19}N_4H_{22}O_7$, and melts at 170°. Its constitution is probably

$$CO[NH\cdot CH(OEt)\cdot C_6H_4\cdot NO_2]_2.$$

The phenylosazone mentioned above forms scarlet crystals slightly soluble in warm water, more readily in alcohol and in ether. It melts at 148°, explodes when heated on platinum foil, and has the formula $NHPh\cdot N\colon CH\cdot C_6H_4\cdot NO_2$. The corresponding meta-compound melts at 153°, the para-compound at 120°. The ortho- and para-compounds are dyes, but not fast. Nitrous acid forms nitroso-derivatives which do not give Liebermann's reaction, and therefore probably have the formula $OH\cdot N(NPh\cdot N\colon CH\cdot C_6H_4\cdot NO_2)_2$. L. T. T.

Amides of Carbonic Acid. By F. EMICH (*Monatsh.*, **10**, 321—353; compare Abstr., 1888, 1063).—All amides of carbonic acid yield cyanates when fused with potash; those containing one or two carbon-atoms (except cyanamidocarbonic acid) only give this reaction when heated with alcoholic potash at 100°. All amides of carbonic acid, when ignited with quicklime, yield cyamide, and many of their derivatives, such as phenylcarbamide, uric and parabanic acids, &c., do the same. These amides do not char on heating, but yield as principal products cyanuric acid, mellone, carbonic anhydride, and

ammonia. The compounds examined were carbaminic acid, cyanuric acid, carbamide, cyanamide, guanidine, biuret, dicyanodiamidine, dicyanodiamide, diguanide, amidocyanic acid, cyanamidocarbonic acid, cyanuric acid, cyanilic acid, cyamelide, melanurenic acid, ammeline, melamine, carbonyldicarbamide, biuretdicyanamide, carbonyldibiuret, melam, melem, ammelide, mellone, cyameluric acid, mellon hydride.
L. T. T.

Rischbieth's γ-Valeroximidolactone. Methylsuccinimide. By J. Bredt and W. Boeddinghous (*Annalen*, **251**, 316—323).—Rischbieth (Abstr., 1888, 44) obtained a product which he termed γ-valeroximidolactone by the action of strong sulphuric acid on isonitrosovaleric acid prepared from levulinic acid and hydroxylamine. As it is well known that isonitroso-compounds prepared by the action of hydroxylamine on γ-aldehydocarboxylic acids yield acid imides when treated with dehydrating agents, the authors have examined Rischbieth's product, and find that it is identical in every respect with methylsuccinimide. W. C. W.

Constitution of Benzene. By A. Claus (*J. pr. Chem.* [2], **40**, 69—77).—In this paper the author criticises the recent work of A. Baeyer on this subject which appeared in *Annalen*, **251**, 257 (see also Abstr., 1888, 1069). A. G. B.

Aromatic Bismuth Compounds. By A. Michaelis and A. Marquardt (*Annalen*, **251**, 323—335).—The preparation of triphenylbismuthine has been described by Michaelis and Polis (Abstr., 1887, 368). This compound is dimorphous, as it exists in two distinct forms belonging to the monoclinic system. Long, thin prisms melting at 78° are deposited from solutions in alcohol or a mixture of alcohol and chloroform. If the alcohol contains a small quantity of bromobenzene, thin plates are occasionally deposited. The tabular crystals melt at 75°. Its sp. gr. is 1·5851 at 20°. *Diphenylbismuthine bromide*, $BiPh_2Br$, is precipitated when ethereal solutions of triphenylbismuthine and bismuth bromide are mixed. After recrystallisation from chloroform, the salt is obtained in yellow crystals. It melts at 157—158°, and is converted into the oxybromide by alcohol. *Triphenylbismuthine dichloride*, $BiPh_3Cl_2$ (*loc. cit.*) melts at 141·5° and the *dibromide* at 122°. The *nitrate*, $BiPh_3(NO_3)_2$ is prepared by adding the theoretical quantity of silver nitrate to an alcoholic solution of the dichloride or dibromide. The precipitate is removed by filtration, and on evaporating the filtrate the nitrate remains in colourless needles. The salt is soluble in chloroform and benzene, and detonates when heated.

A basic carbonate is formed by adding alcoholic sodium hydroxide to an alcoholic solution of the bromide. After removing sodium bromide, carbonic anhydride is passed into the filtrate, when the carbonate is precipitated.

Paratritolylbismuthine closely resembles triphenylbismuthine, and is deposited from a mixture of alcohol and chloroform in long prisms. The compound melts at 120° and is freely soluble in ether, benzene, chloroform, light petroleum, and hot alcohol. The *dichloride* and *dibromide* crystallise in needles, and melt respectively at 147° and

111—112°. The *nitrate*, $Bi(C_7H_7)_3(NO_3)_2$, forms needles or plates sparingly soluble in alcohol. It detonates when heated. *Trixylylbismuthine* $Bi(C_8H_9)_3$, from [1 : 3 : 4] bromoxylene, is freely soluble in benzene and chloroform. It crystallises in needles, and melts at 175°. The *dichloride* forms glistening prisms melting at 161°, and the *dibromide* crystallises in needles and melts at 117°. W. C. W.

Mercury Salicylates. By H. LAJOUX and A. GRANDVAL (*J. Pharm.* [5], **20**, 5—7).—Kranzfeld (*J. Pharm.*, Dec., 1888) has described the preparation of a mercury salicylate. The authors published a paper on the salicylates of mercury in 1882 (*J. Pharm.*). There are two mercurous salicylates, and two mercuric salicylates. The normal mercuric salt prepared by Kranzfeld was prepared by the authors by heating 1 mol. of yellow mercuric oxide with 2 mols, of salicylic acid. The salt obtained had the formula $C_{14}H_4Hg_2O_6$. 1 mol. of acid remains free, and curiously enough, if this molecule in excess is not present, the reaction does not take place. A mercuric nitrate solution precipitated by a solution of normal sodium salicylate gives normal mercuric salicylate, $C_{14}H_5HgO_6$. J. T.

Some Sulphonic Derivatives of Salicylic Acid. By G. PISANELLO (*Gazzetta*, **18**, 346—354).—The formation of monosulphosalicylic acid by the action of sulphuric anhydride on salicylic acid has been already studied by Cahours and others, but the effect of chlorosulphonic acid, which acts so energetically on most aromatic compounds, has not hitherto been examined.

When chlorosulphonic acid is gradually added in slight excess to pure salicylic acid, and the mixture heated in an oil-bath at 180° until hydrogen chloride ceases to be evolved, a heavy brownish-yellow liquid is obtained which, when mixed with water, saturated with barium carbonate, and filtered, yields a solution containing the *barium salt of disulphosalicylic acid* $[C_6H_2(SO_3)_2(OH)\cdot COO]_2Ba_3 + 6\frac{1}{2}H_2O$. This crystallises in small, colourless prisms, sparingly soluble in water, insoluble in alcohol.

Disulphosalicylic acid, $C_6H_2(SO_3H)_2(OH)\cdot COOH, + 4H_2O$, may be obtained from the lead salt by precipitating it with hydrogen sulphide, and evaporating. It forms bundles of minute, colourless, deliquescent needles which melt in their water of crystallisation at 80°; the anhydrous acid melts at 145—146°. With ferric chloride, it gives an intense wine-red coloration, which disappears on the addition of a mineral acid. When fused with potash, it yields phenol and salicylic acid.

Lead disulphosalicylate, $[C_6H_2(SO_3)_2(OH)\cdot COO]_2Pb_3 + 10H_2O$, is obtained from the barium salt by decomposing it with sulphuric acid, neutralising the disulphonic acid with lead carbonate, and evaporating. It forms yellowish prisms, with square base, insoluble in alcohol, sparingly soluble in water. The *cadmium salt* $[C_6H_2(SO_3)_2(OH)\cdot COO]_2Cd_3 + 18H_2O$, crystallises in white, efflorescent prisms. The *copper salt*, with 12 mols. H_2O, forms greenish crystals; the *zinc salt* crystallises in plates with 15 mols. H_2O, the *calcium salt* in needles with 12 mols. H_2O, the *sodium salt* in prismatic needles with 3 mols. H_2O, and the *potassium salt* in rhombic plates, also with 3 mols. H_2O.

When chlorosulphonic acid acts on salicylic acid in molecular proportion at 160°, it gives rise to monosulphosalicylic acid. The author has analysed *cobalt monosulphosalicylate*, which crystallises in rose-coloured prisms with 7 mols. H_2O; the *cadmium salt*, colourless prisms with 8 mols. H_2O, and the *zinc salt* with 3 mols. H_2O.

C. E. G.

Allo-isomerism in the Cinnamic Acid Series. By A. MICHAEL and H. PENDLETON (*J. pr. Chem.* [2], **40**, 63—68; compare Abstr., 1886, 702; 1887, 582).—The authors have obtained Jutz's chlorocinnamic acids by his method (Abstr., 1882, 1073), and find that they melt at 136—137° and 110—111° respectively, instead of 142° and 114°, as given by Jutz. They have also repeated Plöchl's experiments (Abstr., 1883, 194), and obtained chlorocinnamic acid melting at 136—137°, and not 142°. Perkin's method (Trans., 1885, 256) yields an acid melting at 141—142°, as stated by that chemist.

By passing dry hydrogen chloride through a solution of phenylpropiolic acid in cooled glacial acetic acid, and, after a week, pouring it into cold water, a mixture of two chlorocinnamic acids is obtained; their potassium salts may be separated by cold absolute alcohol. The less soluble is the salt of Perkin's acid (m. p. 141—142°); the more soluble is the salt of a new acid, which melts at 132·5°.

A table is given comparing the properties of the four known chlorocinnamic acids.

The authors propose that the acid melting at 132·5° should be regarded as β-chlorocinnamic acid, the acid of m. p. 142° being allo-β-chlorocinnamic acid. Plöchl's synthesis (*loc. cit.*) of the acid melting at 137° shows that it is α-chlorocinnamic acid, analogous to α-bromocinnamic acid; the acid melting at 111° is allo-α-chlorocinnamic acid.

A. G. B.

Phloroglucinotannic Acid. By H. SCHIFF (*Annalen*, **252**, 87—93).—The conversion of phloroglucinolcarboxylic acid into diphloroglucinolcarboxylic acid by the action of phosphorus oxychloride has been already described by the author (Abstr., 1888, 840). When carefully dried diphloroglucinolcarboxylic acid is heated at 160—175°, water is given off, and decomposition sets in. On dissolving the residue in ammonia and fractionally precipitating with hydrochloric acid, *phlorotannin-red*, $C_{14}H_8O_8$, is obtained. This substance is soluble in strong sulphuric acid, but is reprecipitated on diluting the solution with water. It is sparingly soluble in water, and somewhat more soluble in alcohol; the solutions are rendered fluorescent by the addition of an alkali. Phlorotannin-red resembles a quinol in all its properties. It contains four hydroxyl-groups, replaceable by acetyl- or by methyl-groups. The alkaline solution is speedily reduced by sodium amalgam to a colourless liquid, which turns brown on exposure to the air.

Oak-red or oak phlobaphane resembles phlorotannin-red in many of its properties, but its solution in alkalis is not fluorescent. It yields a tetracetic-derivative, $C_{14}H_6O_6Ac_4$. Like phlorotannin-red, the alkaline solution is reduced by zinc-dust or sodium amalgam to a pale yellow liquid, which rapidly oxidises on exposure to the air.

W. C. W.

Derivatives of Anilidosuccinic (Phenyl Aspartic) Acid. By R. Kusserow (*Annalen*, **252**, 158—170).—A solution of bromine in chloroform acts on anhydrous succinimide at 120°, yielding monobromosuccinimide and hydrobromic acid. If water is present, the action takes place at 160°, and monobromosuccinic acid and ammonium bromide are the chief products. Succinic and dibromosuccinic acids are also formed in small quantities. *Monobromosuccinimide* has not been obtained in a pure state. It is a thick oil, which decomposes spontaneously, forming hydrogen bromide, bromofumarimide, and dibromomaleïnimide. Aniline acts energetically on monobromosuccinimide, yielding *anilidosuccinimide*. This compound crystallises in lustrous plates, and melts at 158°. It is soluble in alcohol, and in glacial acetic acid. The *hydrochloride* and the *nitroso*- and *acetic*-derivatives are crystalline. Anilidosuccinimide is converted into anilidosuccinamide by the action of alcoholic ammonia at 100°, and into anilidosuccinamic acid by boiling with milk of lime. *Anilidosuccinanil* is formed by boiling monobromosuccinic acid in aniline. The *nitroso*-compound melts at 180°, and dissolves freely in alcohol and ether. Anilidosuccinanil is converted into *anilidosuccinanilamide* by the action of alcoholic ammonia at 100°. The amide melts at 200°, and dissolves freely in strong acetic acid.

Aniline acts on ethyl bromosuccinate, forming *ethyl anilidosuccinate*, $C_2H_3(NHPh)(COOEt)_2$. This is a highly refractive liquid, boiling at 214° with partial decomposition. The sulphate forms needle-shaped crystals, insoluble in water. Anilidosuccindianilide yields a crystalline nitroso-compound, melting with decomposition at 190°.

W. C. W.

Structural Formulæ of Hydroxylamine and its Derivatives. By W. Lossen (*Annalen*, **252**, 170—240).—The author contends that the hydrogen-atoms in hydroxylamine differ from each other in their behaviour with certain reagents, and consequently that the different affinities of the nitrogen-atom are dissimilar. The question of regarding benzhydroxamic acid as a benzenyl-derivative is discussed at some length. When benzimido-ether is added to hydroxylamine hydrochloride, α- and β-ethylbenzhydroxamic acids and benzenylamidoxime are formed. The product is treated with ether to extract the isomeric ethylbenzhydroxamic acids, and the benzenylamidoxime is precipitated from the residue by sodium hydroxide. The hydrochlorides are precipitated as colourless powders when dry hydrogen chloride is passed into ethereal solutions of the ethylbenzhydroxamic acids. The hydrochlorides decompose on exposure to moist air, yielding ethyl benzoate, but if the dry salts are carefully heated, ethyl chloride and benzhydroxamic acid are formed. The fact that the ethyl salts of α- and β-ethylbenzhydroxamic acids yield the same products when they are subjected to the action of acids, phosphorus pentachloride, ammonia, and potassium hydroxide, shows that, although these compounds are not absolutely identical, they bear the closest possible resemblance to each other. Benzenylamidoxime ethyl ether from ethylic α-ethylbenzhydroxamate is crystallographically identical with the benzenylamidoxime ethyl ether from the β-compound. The ether crystallises in rhombic plates [$a : b : c = 0{\cdot}6935 : 1 : 1{\cdot}9788$]. Benzenylethoximidoethyl ether is identical with the ethyl salts of α- and β-ethylbenzhydroxamic acid, and with the compound formed by introducing the ethyl-group into ethyl benzhydroxamate.

Methyl α-ethylbenzhydroxamate is decomposed by aqueous hydrochloric acid into ethyl benzoate and methoxylamine hydrochloride, and by dry hydrogen chloride into ethyl chloride and methyl benzhydroxamate. Methyl β-ethylbenzhydroxamate yields the same products. Alcoholic ammonia at 160° converts ethyl dibenzhydroxamate into benzamide and ethylbenzhydroxamic acid.

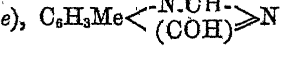
Ethoxyethylamine, NEtH·OEt, is prepared by warming a mixture of ethyl bromide and ethoxylamine; potassium hydroxide is then added to the product, and the liquid is distilled. The distillate boils between 73—96°, and is purified by conversion into the acid oxalate. The crystals of oxalate are drained, washed with a mixture of absolute alcohol and ether, and recrystallised from absolute alcohol. The oxalate melts at 112°, and is soluble in alcohol and in water. It forms triclinic crystals $a : b : c = 0{\cdot}668 : 1 : 0{\cdot}313$; $\alpha = 109^\circ\ 51'$, $\beta = 114^\circ\ 31'$, $\gamma = 77^\circ\ 27'$. A neutral oxalate could not be obtained. The base itself boils at 83°; sp. gr. 0·829 at 0°. It is tolerably soluble in water, and dissolves freely in alcohol and ether. Ethoxyethylamine slowly reduces silver nitrate, and yields amorphous precipitates with copper sulphate and mercuric chloride. The *hydrochloride* is an oily liquid, soluble in alcohol. The *platinochloride*, $2NHEt{\cdot}OEt,H_2PtCl_6$, is obtained in needle-shaped crystals by adding a mixture of benzene and ether to an alcoholic solution of the salt; it melts at 158°. The sulphate is obtained in crystals when benzene is added to the alcoholic solution.

Ethoxyethylamine is decomposed by strong hydrochloric acid at 170°, yielding ethyl chloride and ethylamine. When benzoic chloride is added to an ethereal solution of ethoxyethylamine, ethoxyethylamine hydrochloride is deposited as an oil, and *ethoxyethylbenzamide*, $NEt(OEt){\cdot}C_7H_5O$, remains in the ethereal solution. It is an oily liquid, miscible with alcohol and ether; sp. gr. 1·05408 at 0°. It begins to decompose at 235°, and is slowly converted into benzoic acid and ethoxyethylamine by strong hydrochloric acid at the ordinary temperature This shows that ethoxyethylbenzamide is not identical with ethylic ethylbenzhydroxamate. W. C. W.

Derivatives of Metatoluquinazoline and of Metahomoanthranilic Acid. By S. NIEMENTOWSKI (*J. pr. Chem.* [2], **40**, 1—28; compare Abstr. 1888, 837).—*Orthazoxyparatolunitrile*,

$$CN{\cdot}C_6H_3Me{\cdot}N_2O{\cdot}C_6H_3Me{\cdot}CN\ [CN : N : Me = 1 : 2 : 4],$$

is obtained during the reduction of orthonitroparatolunitrile with tin and hydrochloric acid, or with sodium amalgam in alcoholic solution; it crystallises in stellate, orange-red needles, melting at 182°, and dissolves sparingly in alcohol with a reddish-green fluorescence, more freely in acetone, chloroform, and hot glacial acetic acid.

Anhydroformylorthamidoparatoluylamide (*δ-hydroxymetatoluquinazoline*),  $C_6H_3Me{<}\genfrac{}{}{0pt}{}{-N{:}CH-}{(COH)}{>}N$ [$Me : N : C(OH) = 3 : 5 : 6$], obtained by heating orthamidoparatoluylamide with formic acid, forms small, indistinct crystals, melting at 237—238°, and sparingly soluble in the usual solvents, but easily soluble in alkalis.

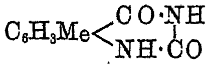
Metahomoanthranilic acid has been already described (Abstr., 1888, 837); the *ammonium*, *silver*, *copper*, and *iron* salts, and the *hydrochloride*, *sulphate*, and *nitrate* are here described.

Orthoformamidoparatoluic acid,

$$COOH\cdot C_6H_3Me\cdot NH\cdot COH\ [Me:NH\cdot COH:COOH = 1:3:4],$$

prepared by heating metahomoanthranilic acid (5 grams) with crystallised formic acid (3 grams), crystallises in very slender, long, white, stellate needles, which begin to melt at 183° and are fully melted at 186—187°; it is sparingly soluble in alcohol and water, insoluble in chloroform and benzene, and soluble in alkalis. By dry distillation it yields water, carbonic oxide, formometatoluide, and a crystalline base which melts at about 140°.

Metamethylorthouramidobenzoyl,



$$C_6H_3Me<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}\ [Me:NH:CO = 3:5:6],$$

(compare this vol., 609), is obtained by heating metahomoanthranilic acid with carbamide (equal mols.) at 200°, also by heating orthamidoparatoluylamide with carbamide at the same temperature; the last method yields the purer product. It crystallises from amyl alcohol in white, stellate needles, and from glacial acetic acid in yellowish, thin, transparent plates; it is sparingly soluble in other solvents, and does not melt at 300°. When cautiously heated, it sublimes unchanged. When distilled with zinc-dust, it yielded a combustible gas, orthamidoparatolunitrile, and an oil which gave a crystalline hydrochloride but was not identified. When heated with iodine and red phosphorus in glacial acetic acid, it yields orthotoluidine.

Nitro-orthacetamidoparatoluic acid, $COOH.C_6H_2Me(NO_2)\cdot NHAc$, obtained when orthacetamidoparatoluic acid is treated at 15—20° with nitric acid of sp. gr. 1·50 (6 parts), crystallises in yellow needles which melt at 210° and are soluble in alcohol, acetone, ether, and chloroform. Ferric chloride gives a yellow precipitate with its aqueous solution.

Nitro-orthamidoparatoluic acid, $COOH\cdot C_6H_2Me(NO_2)\cdot NH_2$. The *potassium* salt of this acid is obtained on saponifying the last mentioned acid with potash; the acid itself crystallises in yellow needles with 1 mol. H_2O; these soften at 240° and melt at 245° with carbonisation; the acid is soluble in alcohol, acetone, ether, and hot water. The *potassium* salt, with 2 mols. H_2O, is described.

A. G. B.

Intramolecular Change of the Oximes of Parachlorobenzophenone, Paratolyl Phenyl Ketone, Phenanthraquinone, and Diphenylene Ketone. By P. Wegerhoff (*Annalen* **252**, 1—44).—*Parachlorobenzophenoneoxime* is freely soluble in ether, alcohol, benzene, and chloroform. It melts at 148—149°. The hydrochloride forms colourless prisms and melts at 110—112° with decomposition. *Paratolylphenylketoxime* forms colourless needles; it melts at 140° and is freely soluble in alcohol, ether, benzene, and chloroform. On exposure to the atmosphere, it slowly deliquesces and decomposes. Both oximes undergo intramolecular change, when subjected to the action of phosphorus pentachloride and water, strong sulphuric acid, or glacial acetic acid saturated with hydrogen chloride. The chief product is the anilide of parachlorobenzoic or paratoluic acid respectively. The behaviour of phenanthraquinonemonoxime under similar treatment has been previously described by the author. (Abstr., 1888, 1200.)

Attempts to bring about a molecular change in phenanthraquinonedioxime anhydride, and in the oximes of diphenylene ketone, and orthodiphenyleneketonecarboxylic acid and amide were unsuccessful.

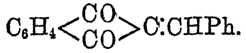
W. C. W.

Intramolecular Change of α- and β-Benzildioxime, α-Benzilmonoxime, and Deoxybenzoinoxime. By E. GÜNTHER (*Annalen*, **252**, 44—72).—The author has previously pointed out (Abstr., 1888, 485) that α-benzildioxime yields the diacetate of β-benzildioxime when it is heated with a solution of hydrogen chloride in glacial acetic acid and acetic anhydride. If acetic anhydride is omitted from the mixture, β-benzildioxime and dibenzenylazoxime are the chief products of the reaction. Dibenzenylazoxime is also formed by the action of strong sulphuric acid, phosphoric anhydride, and phosphorus oxychloride on α-benzildioxime. Phosphorus pentachloride at the ordinary temperature yields a similar result, but at a higher temperature a dichloride, $C_{14}H_{10}N_2Cl_2$ (*loc. cit.*), is formed. The chloride is decomposed by water, yielding benzamide. Silver nitrate eliminates the chlorine from the dichloride and forms a crystalline compound, $C_{14}H_{10}N_2O,AgNO_3$, soluble in alcohol. The silver salt is decomposed by hydrogen sulphide, yielding isodibenzenylazoxime.

Dibenzenylazoxime was first prepared synthetically by Tiemann and Krüger (Abstr., 1884, 1325). β-Benzildioxime yields a small quantity of dibenzenylazoxime when treated with a solution of hydrogen chloride in acetic acid and acetic anhydride, and it is converted into oxanilide by phosphorus pentoxide or pentachloride. Under similar treatment, the α-monoxime is decomposed into benzoic acid and ammonia, and deoxybenzoinoxime is converted by phosphorus pentachloride into phenylacetanilide. W. C. W.

Diketohydrindene. By W. WISLICENUS and A. KÖTZLE (*Annalen*, **252**, 72—79).—The preparation of diketohydrindene has been previously described (Abstr., 1888, 1194). This substance forms a crystalline diphenyldihydrazone which is soluble in alcohol, ether, and benzene and melts at 171°. Ferric chloride imparts a dark-bluish-green coloration to a solution of this compound in strong sulphuric acid.

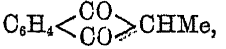
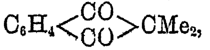
Diketohydrindenedioxime decomposes at 225° and is soluble in alkalis. Isonitrosodiketohydrindene unites with hydroxylamine, forming *tri-isonitrosohydrindene*, a crystalline compound sparingly soluble in alcohol and in water. It melts with decomposition at 197°. Benzaldehyde and diketohydrindene unite together at 120° to form a condensation-product, *benzylidenediketohydrindene*,



$$C_6H_4<\substack{CO\\CO}>C:CHPh.$$

This compound dissolves freely in ether, benzene, warm alcohol, and light petroleum. It melts with decomposition at 150°.

The condensation-product, $C_{18}H_{10}O_3$, obtained by boiling diketohydrindene with water (Abstr., 1887, 587) is most conveniently prepared by boiling the acidified aqueous solution of the yellow sodium compound of ethyl diketohydrindenecarboxylate. An acid solution of this compound dyes wool a violet-red. The monobromo- and dibromo-substitution products are crystalline. The former melts with decomposition at 195—196° and the latter at 241—242°. The mono-derivative is soluble in hot alcohol and gives a violet-red coloration with alkalis. The dibromo-compound is insoluble in alcohol and is decomposed by alkalis. W. C. W.

Action of Ethyl Propionate on Ethyl Phthalate. By W. Wislicenus and A. Kötzle (*Annalen*, **252**, 80—87.—The sodium salt of methyldiketohydrindene is prepared by the action of sodium on a mixture of ethyl propionate and phthalate by a process analogous to that used in the preparation of sodium diketohydrindene (Abstr., 1887, 587). The sodium salt crystallises in small prisms of a dark-red colour. *β-Methyl-α-γ-diketohydrindene*,  $C_6H_4<\substack{CO\\CO}>CHMe$, is deposited from alcoholic solutions in blunt pyramids and from light petroleum in needles. It is also soluble in ether, hot water, and alkalis, melts at 84—85°, and can be distilled without decomposition under a pressure of 18 mm. at about 150°. The *phenylhydrazone* melts at 162—164° and dissolves freely in ether and benzene. The *dioxime* crystallises in needles and melts at 116—117° with decomposition; it is soluble in alcohol, ether, alkalis, and glacial acetic acid. *Methylbromodiketohydrindene* is formed by warming a solution of methylhydrindene in glacial acetic acid with bromine. It crystallises in needles and melts at 90—91°. The crystals dissolve in alcohol, ether, and in alkalis. *Dimethyldiketohydrindene*,  $C_6H_4<\substack{CO\\CO}>CMe_2$, is prepared by the action of methyl iodide on sodium methyldiketohydrindene in presence of methyl alcohol at 100°. This compound melts at 107—108° and boils about 250° with slight decomposition. It is freely soluble in alcohol, ether, and benzene. The *dihydrazone* is deposited from alcohol in slender prisms of a yellowish colour. It melts at 184—187° and is soluble in ether and glacial acetic acid. Ferric chloride gives an intense dark-green coloration to the solution in strong sulphuric acid. W. C. W.

Indole from Phenylamidoacetic Acid. By J. Mauthner and W. Suida (*Monatsh.*, **10**, 250—254; compare Abstr., 1886, 886).—*Calcium phenylamidoacetate*, $(C_8H_8NO_2)_2Ca + 2H_2O$, can be prepared by adding the calculated quantity of milk of lime to a hot aqueous solution of phenylamidoacetic acid and concentrating the filtered solution. It crystallises from 50 per cent. alcohol in broad, colourless needles and is readily soluble in hot water, but almost insoluble in alcohol; it is not decomposed by carbonic anhydride in aqueous solution.

Indole is most conveniently and cheaply prepared by distilling an intimate mixture of calcium phenylamidoacetate and a little more than the calculated quantity of calcium formate; the yield is 5·32 per cent. of the theoretical quantity. The crude distillate is extracted with ether, the extract shaken with dilute acid to free it from aniline, the ether evaporated, and the residue distilled with steam; the aqueous distillate is extracted with ether, the ether evaporated, and the indole separated, by precipitating it with picric acid, from a neutral substance which is also formed in the reaction.

Indole can also be obtained by distilling calcium phenylamidoacetate alone, but the yield is much smaller. F. S. K.

Molecular Refraction of Camphene. By O. WALLACH (*Annalen*, **252**, 136—140).—The author has repeated his determination of the molecular refractions of camphene and pinene, and again finds that the values for these two compounds are almost identical. He is of opinion that Brühl has no grounds for assuming that camphene behaves like a saturated compound. W. C. W.

Isomerism in the Terpene Group. By O. WALLACH (*Annalen*, **252**, 106—136).—The nitrosochlorides of lævo-rotatory and of dextrorotatory limonene can be separated into two isomeric modifications by treatment with cold chloroform; the residue in each case consists of the β-modification. The α-compound is deposited from the filtrate on the addition of methyl alcohol. The crystals are digested in cold ether, and on evaporating the extract α-limonene nitrosochloride separates out in transparent monoclinic crystals

$$a : b : c = 0·78434 : 1 : 1·0395 \beta = 78° 48\tfrac{1}{2}'.$$

The α-nitrosochlorides from dextro- and lævo-limonene are identical in crystalline form, and both melt at 103—104°. The crystals are soluble in an equal weight of chloroform or double their weight of cold ether. The solutions of the two α-nitrosochlorides act on polarised light to an equal extent but in opposite directions.

The crude β-nitrosochlorides are dissolved in 10 times their weight of chloroform. The solution is filtered and mixed with methyl alcohol, the precipitate is washed with a small quantity of ether, dried, and again treated with ether. The residue is the pure β-compound. The β-nitrosochlorides are less soluble than the α-compounds, and their action on polarised light is feeble. The β-nitrosochloride of lævolimonene melts at 100°; that of dextro-limonene at 105—106°. The α- and β-nitrosochlorides are physical isomerides; they are chemically identical, as they unite with bases to form the same compounds.

Two isomeric compounds are obtained by warming a mixture of piperidine (20 grams), lævo-α-limonene nitrosochloride (20 grams), and alcohol (60 c.c.). When complete solution is effected, a small quantity of water is added to the warm liquid and it is left to crystallise. Impure β-nitrolpiperidine is deposited, and on the addition of water to the mother liquor crude α-nitrolpiperidine is precipitated. The α-compound is dried and treated with a small quantity of cold, light petroleum, the solution evaporated, and the residue recrystallised from alcohol. The β-compound is treated with cold, light petroleum, and the residue is recrystallised from warm, light petroleum. *Limonene-α-nitrolpiperidine* crystallises in the rhombic system, $a : b : c = 0{\cdot}82973 : 1 : 0{\cdot}7745$, and melts at 93—94°. It dissolves freely in ether, chloroform, and light petroleum, but is less soluble in alcohol. These solutions are lævo-rotatory. The hydrochloride is very soluble in water; the solution is dextro-rotatory. *Limonene-β-nitrolpiperidine* melts at 110—111. It crystallises in the monoclinic system, generally in twin crystals. Solutions of this compound are dextro-rotatory. The solution of the hydrochloride is almost optically inactive. The α- and β-nitrolpiperidine from dextro-limonene bear a close resemblance to the corresponding derivatives of lævo-rotatory pinene in their crystalline form and melting points. The solution of the α-compound is dextro-rotatory; that of the hydrochloride lævo-rotatory. The β-derivative is lævo-rotatory.

Each of the limonene nitrosochlorides yields two isomeric anilides. These compounds are prepared by warming a mixture of aniline, alcohol, and limonene nitrosochloride, and precipitating with water. The crude product is treated with strong hydrochloric acid, which dissolves the β-compound, and the residue is dissolved in boiling water. On cooling, the α-hydrochloride crystallises out. It is decomposed by ammonia and the free base extracted with ether. The α-anilide melts at 112—113°. Small quantities of impurities prevent the base from crystallising. The α-anilide from the dextro-nitrosochloride is dextro-rotatory, that from the lævo-nitrosochloride is lævo-rotatory, but in other respects the compounds are identical. The hydrochlorides are only sparingly soluble in water, but more freely in alcohol; their action on polarised light is much less powerful than that of the bases. The β-anilides melt about 153—154°. The rotatory power of the β-bases is about 80°. The β-base from the dextro-nitrosochloride is lævo-gyrate and that from the lævo-nitrosochloride is dextro-gyrate.

Two isomeric bases are also formed by the action of α-limonene nitrosochloride on benzylamine, but only the α-base could be isolated in a pure state. This is effected by recrystallising the crude product from alcohol. *α-Limonenenitrolbenzylamine* melts at 93°. The base from dextro-limonene is dextro-rotatory, that from lævo-limonene lævo-rotatory. The salts are crystalline, and are soluble in dilute alcohol, but only sparingly soluble in water. Their action on polarised light is the reverse of that of the bases.

α-Dipentene nitrosochloride is prepared synthetically by mixing equal weights of dextro- and lævo-limonene nitrosochloride in ethereal solution. A small quantity of methyl alcohol is added, and the mixture slowly evaporated. The product melts at 103—104°. When equal weights of dextro- and lævo-limonene α-nitrolpiperidide in solution in light petroleum are mixed, inactive *α-dipentenenitrolpiperidine* is deposited. It melts at 154°, and is sparingly soluble in most solvents. The corresponding β-compound melts at 152°, and is more soluble than the α-compound. Inactive *α-dipentenenitrolaniline* melts at 125—126°, and the β-derivative melts at 149°. *α-Dipentenenitrolbenzylamine* forms monoclinic plates, $a : b : c = 0{\cdot}77227 : 1 : 036393$ $\beta = 78° 29'$. It melts at 109—110°.

The rotatory power and melting points of the dipentene-derivatives and of the limonene compounds from which they are built up are shown in the following table:—

	Nitrolamines from						
	Lævo-limonene.		Dextro-limonene.		Dipentenes.		
		R°.	M. pt.	R°.	M. pt.	R°.	M. pt.
With piperidine	α	−	94°	+	94°	0	154°
	β	+	110	−	110°	0	152
With aniline ..	α	−	112	+	112	0	125
	β	+	153	−	153	0	149
Benzylamine ..	α	−	93	+	93	0	110

Pinenenitrolbenzylamine from dextrogyrate or from lævogyrate oil of turpentine forms hemihedral rhombic crystals

$$a : b : c = 0{\cdot}85912 : 1 : 0{\cdot}94228.$$

It is optically inactive and melts at 122—123°. The hydrochloride crystallises in prisms. Pinene nitrosochloride acts on aniline, forming amidazobenzene hydrochloride.

Terpinenenitrolbenzylamine is prepared by warming a mixture of terpinene nitrosite, benzylamine, and alcohol; on adding water, the base is precipitated in an impure state. It can be purified by dissolving the crude product in strong acetic acid, and diluting with water, when a resinous impurity is precipitated; the addition of ammonia to the filtrate precipitates the base, which is recrystallised from warm alcohol. It melts at 137°, and forms a crystalline hydrochloride soluble in water. *Sylvestrenenitrolbenzylamine* melts at 71—72°. Solutions of this compound are dextro-rotatory. W. C. W.

Rotatory Power of Terpine-derivatives. By O. Wallach and E. Conrady (*Annalen*, **252**, 141—157).—The optical behaviour of certain limonene-derivatives is shown in the following table:—

	Prepared from	
	Lævo-limonene.	Dextro-limonene.
Limonene, $C_{10}H_{16}$	−105·00°	+106·8°
,, tetrabromide, $C_{10}H_{16}Br_4$	−73·45	+73·27
,, α-nitrosochloride, $C_{10}H_{16},NOCl$	−314·8	+313·4
,, β-nitrosochloride, $C_{10}H_{16},NOCl$	−242·2	+240·3
,, α-nitrolpiperidine, $C_{10}H_{16},NONC_5H_{10}$	−67·60	+67·75
,, β-nitrolpiperidine, $C_{10}H_{16},NONC_5H_{10}$	+60·18	−60·48
,, α-nitrolbenzylamine, $C_{10}H_{16},NONHC_7H_7$	−163·6	+163·8
,, α- ,, hydrochloride	+83·06	−82·26
,, α- ,, nitrate	+81·0	−81·5
,, α- ,, dextro-tartrate	+69·6	−49·9
,, α- ,, lævo-tartrate	+51·0	−69·9
Carvoxime, $C_{10}H_{14}{\cdot}NOH$	+39·71	−39·34
Benzoylcarvoxime, $C_{10}H_{14}{\cdot}NOBz$	+26·47	−26·97

Sylvestrene, $C_{10}H_{16}$	+66·32°
,, dihydrochloride	+18·99
,, dihydrobromide	+17·89
,, tetrabromide	+73·74
,, nitrolbenzylamine	+185·6
,, nitrolbenzyl hydrochloride	+79·2
Sesquiterpene	−98·56
,, dihydrochloride	−36·82
,, dihydrobromide	−36·13
,, dihydriodide	−48·00

The hydrobromide and hydrochloride of dextro-pinene are optically inactive. The corresponding compounds of lævo-pinene are dextrorotatory.
W. C. W.

Terpenes and Ethereal Oils. Part II. By O. Wallach (*Annalen*, **252**, 94—105).—Brühl (Abstr., 1888, 377) examined the molecular refraction of numerous essential oils, and arrived at the conclusion that laurene and menthene are not identical with any known terpenes. The author has re-examined the oil obtained from the leaves and from the berries of the laurel, and finds that it consists of a mixture of cineole and pinene. Olibene from frankincense is identical with lævo-pinene. Elemi oil contains dextro-phellandrene, dipentene, and a crystalline compound, which is probably Vesterberg's amyrin (Abstr., 1887, 733). The lower boiling fraction of oil of sage contains pinene and cineole, but the chief portion boiling between 201 and 204° consists of salviole. The portion of mace oil boiling about 165° consists of a mixture of dextro- and lævo-pinene. The higher boiling fractions contain dipentene, and a dextro-rotatory compound which has not yet been investigated.
W. C. W.

Bay Oil (Oleum Myrciæ acris). By O. Mittmann (*Arch. Pharm.*, [3], **27**, 529—548).—The oil was dark yellow to brown in colour, had a sharp taste, an odour somewhat resembling that of cloves, and a sp. gr. of 0·970 at 15°. It was soluble in ether, light petroleum, carbon bisulphide, and chloroform, but became turbid with alcohol and other substances easily miscible with water. The oil contained neither sulphur nor nitrogen; its reaction was neutral to litmus. Ferric chloride in presence of alcohol produced a blue coloration, indicating the presence of phenols. Aqueous potassium hydroxide extracted a substance soluble in alcohol, which gave a strong blue coloration with ferric chloride. A silver mirror was produced with alcoholic ammoniacal silver solution. Aldehydes and ketones were not found. After removing mechanically admixed water by means of anhydrous sodium sulphate, and distilling, a portion came over between 160° and 200°, which was clear, colourless, and highly refracting; this did not colour ferric chloride, faintly reduced silver solution, and was not acted on by alcoholic potash. Between 210° and 250°, a colourless oil passed over, which became brown on exposure to air, gave a blue coloration with ferric chloride in alcoholic solution, strongly reduced silver solution, and immediately solidified with alcoholic potassium hydroxide. This second portion was considerably larger than the first. Dissociation commenced a little above 250°. All the distillates were soluble in alcohol, but the residue in the retort was only soluble in ether, light petroleum, chloroform, &c. The separate portions were further examined and were resolved into (*a*) the three terpenes, pinene, very probably dipentene, and a polyterpene, probably diterpene; (*b*) eugenol; and (*c*) the methyl ether of the foregoing. J. T.

Synthesis of Hydropyridic Bases. By A. and C. COMBES (*Bull. Soc. Chim.* [3], 1, 14—16).—By a reaction analogous to that yielding quinoline-derivatives (Abstr., 1888, 504), a dihydrodiacetylcollidine, $C_{12}H_{17}NO_2$, may be prepared. Aldehyde ammonia (1 mol.) is heated with acetylacetone (2 mols.) for one hour in a water-bath. The solid product obtained, crystallises from alcohol in transparent, yellow, hexagonal prisms melting at 153° and distilling under reduced pressure at 250°; the hydrochloride is crystalline, the aurochloride and platinochloride are very unstable, and the base itself is insoluble in water. T. G. N.

Constitution of the Cinchona Alkaloïds. By Z. H. SKRAUP and J. WÜRSTL (*Monatsh*, **10**, 220—230; compare *Monatsh.*, **10**, 65, this vol., p. 626).—It has been previously shown that quinidine, on oxidation, yields cincholeuponic acid and quininic acid; the authors have now succeeded in isolating pure cincholeupone hydrochloride from the crude oxidation-product, and find it to be identical in every respect with the corresponding compound obtained from quinine and cinchonidine.

Cincholeupone is also formed when cinchonidine is oxidised with chromic acid. The mercurochloride can be isolated by repeatedly precipitating with mercuric chloride, and extracting the precipitate with boiling water; the hydrochloride, obtained by decomposing the double salt with hydrogen sulphide, is identical in chemical and optical properties with the corresponding compound obtained from cinchonine, quinine, and quinidine.

Quinicine, prepared by heating quinine hydrogen sulphate, was oxidised, and the crude product investigated exactly as has been previously described in the case of the other alkaloïds. Considerable quantities of quininic acid, cincholeuponic acid hydrochloride, and cincholeupone hydrochloride, identical in chemical and physical properties with the corresponding compounds obtained from quinine and quinidine, were isolated.

Cinchonicine on oxidation yields cincholeuponic acid, identical with the acid obtained from cinchonine and cinchonidine; cincholeupone has not yet been isolated from the oxidation-products, but that it is actually present is more than probable.

The investigation of the cinchona alkaloïds has shown that not only the four naturally occurring bases quinine, quinidine, cinchonine, and cinchonidine, but also the amorphous compounds quinicine and cinchonicine formed therefrom by intramolecular change, are so similar in constitution that the only difference in their decomposition-products is due to a difference in the empirical formulæ of the alkaloïds. All six bases contain one and the same group of atoms, from which, on oxidation, cincholeupone is formed. Although the rotatory power of cincholeupone has not yet been determined, it must contain a dextro-rotatory group of atoms, because, on oxidation, it is converted into cincholeuponic acid ($[\alpha]_D = + 35° 61'$). Pasteur's hypothesis (*Jahresb.*, 1853, 474) as to the cause of the peculiar optical properties of the cinchona alkaloïds is fully borne out by the facts which have hitherto been brought to light.

Quinine, quinidine, and quinicine are most probably identical in structure and stereo-chemically isomeric, as are also cinchonidine, cinchonine, and cinchonicine. The first members of the two groups are analogous to lævo-tartaric acid, the next to dextro-tartaric acid, and the last numbers are analogous to optically-inactive tartaric acid. The analogy is, however, incomplete, as the optical activity of the alkaloïds does not cease entirely when intramolecular change takes place. The cinchona alkaloïds contain at least two, and, according to the researches of Jungfleisch and Léger (*Compt. rend.*, **105**, 1257), in all probability more than two, asymmetric carbon-atoms.

F. S. K.

Alkaloïds of Mandragora. By F. B. Ahrens (*Annalen*, **251**, 312—316).—*Mandragorine* is extracted from the powdered roots of the mandragora by maceration with alcohol; the extract is evaporated, and the residue treated with very dilute acid. The alkaloïd is liberated from the acid solution by adding an excess of potassium carbonate and extracting with ether. It is a hygroscopic, brittle resin, melting about 77—79°. The sulphate is crystalline and deliquescent. A small quantity of the solution dropped into the eye causes dilation of the pupil. The *aurochloride*, $C_{17}H_{23}NO_3,HAuCl_4$, forms yellow plates exhibiting a fatty lustre. The salt is soluble in hot water and in water containing hydrochloric acid. It melts at 153—155°. The platinochloride melts at 194—196° with decomposition. Mandragorine is not converted into atropine by alkalis.

Hydrochloric acid extracts a second alkaloïd from the residue of the mandragora root from which the mandragorine has been removed.

It has not been obtained in a solid state, but the platinochloride and the aurochloride are crystalline. The former melts at 179—181°, and the latter begins to melt at 147°, becoming completely fused at 153°.

W. C. W.

New Ptomaïne. By A. M. Delèzinier (*Bull. Soc. Chim.* [3], 1, 178—180).—The ptomaïne discovered by Brouardel and described by him as both chemically and physiologically analogous to veratrine (*Moniteur scient.* [3], 10, 1140) has been prepared in quantity by the author. Only when in contact with air does the analogy to veratrine obtain, and an apparatus is described by means of which the reactions are studied in an atmosphere of nitrogen.

This ptomaïne, which appears to be a secondary monamine, $C_{32}H_{31}N$, is an almost colourless oily liquid having a hawthorn-like odour. It is insoluble in water, but alcohol, ether, toluene, and benzene dissolve it readily. It is extremely oxidisable, and forms salts which are very deliquescent.

T. G. N.

Proteïds of White of Egg. By G. Corin and E. Berard (*Archiv. de Biol.*, 9, 1—16).—The proteïds of white of egg were examined by the method introduced by Halliburton (*J. Physiol.* 5) in the investigation of the proteïds of serum. The method is that of fractional heat coagulation, the solution being kept throughout very faintly acid. The solution of white of egg, after filtration, was usually acid; this was neutralised with solution of potassium hydroxide (1 in 1,000) until phenolphthaleïn paper was reddened, and then to each 5 c.c. of the solution one drop of 2 per cent. acetic acid was added. After the formation of a heat coagulum, the lessening of acidity was corrected by the addition of more acid. A water-bath with an Elster's gas regulator served for heating the solutions. A proteïd always becomes opalescent before it is precipitated by heat, and in the case of egg proteïds at least, it is not correct to distinguish between the temperature at which opalescence occurs and the coagulation temperature, for, if the liquid be allowed to remain for a sufficient length of time (two hours in most cases) at the lower temperature, the opalescent solution becomes filled with a flocculent precipitate.

The results obtained are as follows:—There exist in white of egg two kinds of proteïds—

1.—Those coagulable by heat; of which two belong to the globulin class, and are precipitable by saturation with magnesium sulphate. Their coagulation temperatures are:—oviglobulin α at 57·5°; oviglobulin β at 67°. There are in addition three members of the albumin class which coagulate at the following temperatures: albumin α at 72°, β at 76°, and γ at 82°.

2.—Peptones, which increase in amount with the staleness of the egg. Their presence does not influence the coagulation temperature of the other proteïds.

The colouring matter of the white of egg is, like the peptone, not coagulated by heat.

When a solution of albumin is raised to such a temperature that opalescence sets in, it becomes precipitable by saturation with magnesium sulphate, like a globulin. It is possible that albumin, immediately before its coagulation, passes into an intermediate condition in which it has the composition and properties of a globulin.

W. D. H.

Physiological Chemistry.

Feeding of Milch Cows. By N. J. Fjord (*Bied. Centr.*, 1889, 517—525).—The cows were selected in groups of 10 on several large farms, and fed with a mixture of palm cake, rape cake, bran, barley and oat chaff, clover, hay, and straw *ad lib.* To this food was added during the period of preparation 4½ kilos. of red beet and 4½ kilos. of turnips; this was increased in the actual period of experiment to 18 kilos. of roots. It was then observed that the addition of roots had no effect on the composition of the milk, and the evening milk was always found to be richer in fat than that of the morning; the beet, however, produced a greater increase in live weight than the turnips did.

E. W. P.

Coagulation of the Blood. By L. C. Wooldridge (*J. Physiol.*, **10**, 329—340).—A further reply to criticisms by Halliburton (Abstr., 1888, 974; this vol., pp. 63, 288).

Nitrogen in Sputum. By M. Panoff (*Dissertations Med.-Chi. Acad. St. Petersb.*, 1888—89, *No.* 2). By estimating the nitrogen in the sputum of patients suffering from various lung diseases by means of the Kjeldahl-Borodin process, it is found that both the total amount per diem and the relative amount of nitrogen in the sputum is greatest in phthisis and least in bronchitis and croupous pneumonia.

T. M.

Horse Fat. By L. Lenz (*Zeit. anal. Chem.*, **28**, 441—443).—A fresh specimen, extracted in the laboratory, having a melting point of 20°, and of the composition C 76·72, H 12·17, O 11·17 per cent., insoluble fatty acids 95·68 per cent., was exposed to air, and weighed periodically during two years. It remained unchanged for the first four weeks. It then began to gain in weight. In the course of the first year it gained 2·707 per cent., and in the second 0·788, thereafter remaining unaltered. Its composition was then C 71·05, H 10·95, O 18·0 per cent.; insoluble fatty acids 90·54 per cent. It was rancid; 100 grams neutralised 34 c.c. of normal alkali.

M. J.

Physiological Action of Acetophenone. S. S. Karmenski (*Diss. Med.-Chi. Acad. St. Petersb.*, 1888—1889, *No.* 70).—Acetophenone lowers sensation and reflex action, produces sleep, slows the heart, apparently by acting on the accelerator apparatus, increases the irritability of the respiratory centre, except in large doses, which destroy it entirely, lowers the blood pressure by affecting the vasculo-motor centre and by weakening the heart, lowers the irritability of the brain, in medium and large doses, and that of the spinal cord in all doses, and lowers the temperature of the body. T. M.

Chemistry of Vegetable Physiology and Agriculture.

Nutritive Value and Produce of Grasses and Clovers. Part II. By D. WILSON (*Trans. High. and Agr. Soc. of Scotland*, 1889 [5], **1**, 1—45).—Seventeen plots of grasses and clovers grown in 1885 yielded the results already recorded (Abstr., 1886, 906). The growth of these plots has been watched during the three subsequent years, and plots of several grasses and leguminous plants not included or not succeeding in the first series have been laid down, and the produce collected and analysed. Three cuttings of the crops were taken, at periods corresponding with those of the first series, and the methods of analysis and of valuation were likewise the same, and have been described in the Abstract above cited. The results for the grasses and plants not included in the former series are here condensed and tabulated on the plan then adopted.

Tall oat grass (*Arrhenatherum avenaceum*) is one of the most productive at all seasons, and is at least permanent enough for a two or three years ley. It is exceptional in not deteriorating between the time when the grass begins to shoot and the time when the seed is full sized. No loss is sustained in delaying the cutting until the clovers are in bloom.

Fiorin (*Agrostis stolonifera latifolia*) has no exceptional quality to recommend it. Although said to grow better in late autumn than any other, in these experiments, cocksfoot, golden oat grass, and tall oat grass surpassed it in late as well as in early growth, besides being more productive during the summer.

Various leaved fescue (*Festuca heterophylla*) is on the whole inferior to hard fescue, and throws up more wiry stems, with less undergrowth.

Smooth stalked meadow grass (*Poa pratensis*) stands heat and cold better than the rough stalked, and yields a greater weight of dry food at all the cuttings, but a little of the latter should be included in mixtures, because sheep are so fond of the young shoots, and it has such a power of filling up interstices in a pasture.

Floating sweet-grass (*Glyceria fluitans*) continued growing later in the year than any other grass. All the cuttings were taken before the blooming period; no grass produced young leaves of greater nutritive value, and the bright green leaves forming the first and third cuttings of portion A were exceptionally rich in albuminoids, and low in woody fibre. It is suitable for moist land, and a good addition to mixtures for retentive pastures.

I.—*First Cutting of Portions A, on June 10th*, 1887, *and June 11th*, 1888.*

Composition of the fresh herbage.	Tall oat grass.	Fiorin.	Various leaved fescue.	Smooth stalked meadow.	Hungarian forage grass.	Floating sweet grass.	Reed canary grass.	Wood fescue.	Perennial red clover.	Dutch clover.	Alsike clover.	Lucerne.
Water	74·11	77·27	73·20	66·55	78·13	78·47	82·60	81·38	85·41	85·92	85·37	84·84
Digestible albuminoïds	0·97	1·56	1·21	1·63	1·32	2·23	1·26	0·79	1·27	1·51	1·35	1·36
Indigestible albuminoïds	0·60	0·88	1·04	0·88	0·67	0·64	0·60	0·47	0·63	0·60	0·62	0·53
Non-albuminoïd N × 6·25	0·58	0·52	0·71	0·48	1·03	1·22	1·12	0·83	0·86	0·49	0·80	1·57
Fat, wax, and chlorophyll	0·56	0·62	0·83	0·82	0·45	0·96	0·55	0·36	0·55	0·42	0·41	0·34
Extractive matter free from nitrogen	12·69	10·21	12·27	17·05	10·20	11·39	8·33	9·11	6·07	6·46	6·83	6·07
Ash	1·70	2·17	2·00	2·42	2·52	1·78	2·01	1·67	2·01	2·07	1·71	1·94
Woody fibre	8·79	6·77	8·74	10·17	5·68	3·31	3·53	5·39	3·20	2·53	2·91	3·35
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Weight of given crop	1102	384	369	380	570	242	961	910	1758	725	1700	515
Containing dry matter	250	83	90	92	125	52	167	169	256	102	249	78
= Hay with 14·3 per cent. water	292	97	105	107	145	61	195	198	299	119	290	91
Containing albuminoïds	15·15	8·89	7·54	6·90	11·34	6·96	17·84	11·48	33·44	15·25	33·45	9·73
Percentage of total nitrogen non-albuminoïd	26·8	17·8	24·0	16·0	34·1	29·9	37·7	39·8	31·1	18·9	28·8	45·4
Percentage of total albuminoïds, digestible	61·6	67·8	53·8	65·1	66·4	77·6	67·6	62·5	67·0	71·5	68·6	71·9
Albuminoïd ratio: 1 to	8·6	4·6	6·0	7·3	5·4	4·4	4·9	7·6	3·6	3·4	3·8	3·4
Comparative value, cocksfoot, 1st cut = 100	94	121	105	104	115	157	131	101	140	151	145	142
Value of produce	2350	1004	945	957	1434	818	2190	1711	3583	1540	3611	1109

II.—*Third Cutting of Portions A, on October 17th,* 1887, *and October 15th,* 1888.

Composition of the fresh herbage.	Tall oat grass.	Fiorin.	Various leaved fescue.	Smooth stalked meadow.	Hungarian forage grass.	Floating sweet grass.	Reed canary grass.	Wood fescue.	Perennial red clover.	Dutch clover.	Alsike clover.	Lucerne.
Water	76·62	74·78	74·79	70·99	80·06	71·69	82·12	78·47	80·99	72·49	80·35	81·09
Digestible albuminoïds	1·38	1·56	1·68	2·40	1·72	2·97	1·77	1·53	2·08	3·28	2·48	1·85
Indigestible albuminoïds	0·67	1·07	1·37	0·78	0·80	1·06	0·75	0·80	0·80	1·27	0·91	0·77
Non-albuminoïd N × 6·25	0·83	0·50	1·05	1·03	0·87	0·89	0·77	0·75	0·77	1·07	0·67	1·37
Fat, wax, and chlorophyll	0 93	0·86	0·89	0·88	0·87	1·05	0·93	0·82	0·73	0·78	0 82	0·48
Extractive matter free from nitrogen.	11·36	10·86	11·45	14·49	8·35	15·01	6·87	9·87	9·06	14·70	9·32	7·39
Ash	2 39	2·87	2·71	3·20	2·65	2·48	2·85	2·85	2·15	2·99	2·22	2·46
Woody fibre	5·82	7 50	6·06	6·23	4·68	4·85	3·94	4·91	3·42	3·42	3·23	4·59
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100 00
Weight of green crop	504	165	134	105	138	101	326	389	420	21	81	392
Containing dry matter	112	44	34	30	27	29	58	84	80	6	16	74
= Hay with 14·3 per cent. water	131	52	39	35	32	33	68	98	93	7	19	86
Containing albuminoïds	9·82	4·58	4·11	3·29	3·48	4·07	8 22	9·05	12·08	0·96	2 75	10·30
Percentage of total nitrogen non-albuminoïd	28·9	15·9	25·6	24·4	25·7	18·1	23 4	24·3	21·2	19·0	16·4	34·4
Percentage of total albuminoïds, digestible	67·2	59·5	55·2	75·5	68 0	73 7	70·1	65·5	72·2	72 2	73·2	70·5
Albuminoid ratio: 1 to	5·9	4·4	4·0	4·8	3·6	3 9	3·0	4·5	3·4	3·4	3·0	3·0
Comparative value, cocksfoot, 1st cut = 100	114	112	127	130	133	153	142	123	155	167	167	142
Value of produce	1276	493	432	390	366	437	822	1030	1210	97	267	1053

III.—*First Cutting of Portions B, on July 6th*, 1887 *and* 1888.

Composition of the fresh herbage.	Tall oat grass.	Fiorin.	Various leaved fescue.	Smooth stalked meadow.	Hungarian forage grass.	Floating sweet grass.	Reed canary grass.	Wood fescue.	Perennial red clover.	Dutch clover.	Alsike clover.	Lucerne.
Water	61·14	65·25	61·17	57·65	66·15	75·68	72·93	79·21	73·01	76·41	71·13	78·36
Digestible albuminoïds	1·27	1·00	1·87	1·38	1·57	1·19	1·39	1·16	1·65	1·23	1·86	2·17
Indigestible albuminoïds	1·00	0·90	1·19	1·40	0·66	0·74	0·68	0·45	1·38	1·27	0·85	0·68
Non-albuminoïd N × 6·25	0·33	0·59	0·46	0·91	0·48	0·93	0·97	0·36	1·41	0·96	1·01	1·45
Fat, wax, and chlorophyll	1·06	0·66	0·58	0·52	0·38	0·56	0·59	0·34	0·67	0·52	0·74	0·37
Extractive matter free from nitrogen.	21·05	18·66	19·81	22·26	17·70	13·12	11·13	10·99	13·17	11·97	15·52	7·90
Ash	2·49	3·09	2·82	3·01	2·30	1·77	2·41	1·58	2·43	3·03	2·38	2·68
Woody fibre	11·66	9·85	12·10	12·87	10·76	6·01	9·90	5·91	6·28	4·61	6·51	6·39
	100·00	100·00	100·00	100 00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Weight of green crop	1152	740	473	353	936	648	1783	1293	1665	966	1635	1058
Containing dry matter	418	229	159	136	317	158	483	269	449	228	472	229
= Hay with 14·3 per cent. water	487	267	185	158	370	184	563	314	524	266	551	267
Containing albuminoïds	24·50	12·48	12·56	8·91	20·84	12·56	36·93	20·86	50·41	24·17	44·25	30·09
Percentage of total nitrogen non-albuminoïd	12·7	23·9	13·1	24·8	17·6	32·4	32·0	18·2	31·8	27·8	27·2	33·8
Percentage of total albuminoïds, digestible	55·8	52·5	61·2	49·6	70·6	61·6	67·2	71·9	54·4	49·4	68·7	76·2
Albuminoïd ratio: 1 to	9·7	10·2	6·6	8·2	8·2	7·3	5·7	7·1	4·6	5·0	6·0	2·9
Comparative value, cocksfoot, 1st cut = 100	94	91	102	95	97	113	98	107	127	121	123	136
Value of produce	3929	2084	1622	1292	3073	1781	4730	2877	5702	2758	5805	3114

IV.—*Average Total Produce for the Season of Portions A.*

	Tall oat grass.	Fiorin.	Various leaved fescue.	Smooth stalked meadow.	Hungarian forage grass.	Floating sweet grass.	Reed canary grass.	Wood fescue.	Perennial red clover.	Dutch clover.	Alsike clover.	Lucerne.
1st cutting, June 10th, 1887, and June 11th, 1888	1102	384	369	380	570	242	961	910	1758	725	1700	515
2nd cutting, August 14th, 1887, and August 14th, 1888	433	361	199	213	488	429	1029	470	639	161	217	760
3rd cutting, October 17th, 1887, and October 15th, 1888	504	165	134	105	138	101	326	389	420	21	81	392
Total weight green crop............	2039	910	702	698	1196	772	2316	1769	2817	907	1998	1667
Containing dry matter	487	226	179	191	279	193	528	390	448	147	308	365
= Hay with 14·3 per cent. water....	569	265	207	223	325	224	617	456	522	172	359	426
Containing albuminoïds	34·31	23·15	17·59	17·60	26·01	18·57	56·52	35·06	62·41	21·88	43·42	47·46
Value of produce..................	4926	2625	2026	2106	3168	2382	6438	4330	6447	2198	4549	4977

V.—*Average Total Produce for the Season of Portions B.*

	Tall oat grass.	Fiorin.	Various leaved fescue.	Smooth stalked meadow.	Hungarian forage grass.	Floating sweet grass.	Reed canary grass.	Wood fescue.	Perennial red clover.	Dutch clover.	Alsike clover.	Lucerne.
1st cutting, July 6th, 1887, and July 6th, 1888	1152	740	473	353	936	648	1783	1293	1665	966	1635	1058
2nd cutting, Sept. 19th, 1887, and Sept. 19th, 1888	687	372	187	262	645	376	969	697	1211	298	682	1128
3rd cutting, Oct. 17th, 1887, and Oct. 15th, 1888	19	4	11	—	—	—	—	19	23	—	—	36
Total weight green crop	1858	1116	671	615	1581	1024	2752	2009	2899	1264	2317	2222
Containing dry matter	608	340	212	209	476	243	721	466	686	286	604	422
= Hay with 14·3 per cent. water	708	397	246	243	555	284	840	544	801	334	705	492
Containing albuminoïds	42·52	20·86	17·40	16·30	30·98	21·40	53·40	32·43	82·39	31·97	63·73	49·24
Value of produce	5947	3228	2210	2146	4536	2790	7060	4746	8916	3570	7745	5335

Hudson's Bay grass (*Poa nemoralis sempervirens*) was sown, but no difference could be detected between its produce and that of the plot of wood meadow grass (*P. nemoralis*) sown in 1884; also the differences between red fescue (*Festuca rubra*) and the 1884 plot of hard fescue, and between sheep's fescue (*F. ovina*) and the old plot of fine-leaved sheep's fescue, were so slight that these grasses were not analysed.

Reed canary grass (*Phalaris arundinacea*) favoured by the wet and sunless season (1888) gave a greater yield than that of any other plot during the four years of experiment; the "total value of its produce" was a half greater than the four years' average of cocksfoot. It flowers about a month later than cocksfoot, and at the same stage their nutritive values are about the same, but after blooming it becomes very woody. It deserves a trial in moist or irrigated meadows, to yield two or three cuts of green stuff, or to fill a silo.

Hungarian forage grass, or smooth awnless brome grass (*Bromus inermis*) is best suited for dry, thin soils, where most of the other strong-growing grasses are out of place. It flowers a month later than cocksfoot, and is a little inferior in nutritive quality.

Wood fescue (*Brachypodium sylvaticum*) grew as rapidly as reed canary grass up to the beginning of June, but was afterwards much less productive, and its nutritive value, especially in the young leaves, is greatly inferior to that of the former.

As regards the clovers (the new sowings of which stood the first winter much better than the first series), whilst alsike yielded as much at the first cuttings (A and B) as perennial red, the aftermaths of the latter were twice as heavy. Dutch clover cannot compete with the larger ones in weight of produce, but all the cuttings of it contained the least woody fibre. The value of produce for the season is greatest in red clover, and is greater in all when first cutting is delayed until blooming, for clovers do not deteriorate so rapidly as grasses. Lucerne in moderately deep soils is a useful addition to fill up the deficiency between the dying out of the clovers sown and the reappearance of the natural white clover; it grows so rapidly after cutting that it should never be allowed to flower.

The produce of the plots sown in 1884 has been weighed every year since, and the following observations supplement or modify those made in that year. The produce of sweet vernal grass has decreased every season. Crested dogstail also has fallen off in yield. Golden oat grass, wood meadow grass, and hard fescue have increased in productiveness; the first-named grows more rapidly in August and September than any of the other permanent grasses. Meadow fescue has fallen off slightly in yield, but the very nutritious quality of its young leaves entitles it to be called, perhaps, the best grass for permanent pasture. The leaves of tall fescue have become rather coarser each year.

The productiveness of cocksfoot, meadow foxtail, and timothy was fairly represented by the first season's results. The high opinion of the nourishing quality of foxtail is confirmed by experience in the pastures. Cocksfoot, one of the earliest and most productive grasses, is one of the most difficult to graze satisfactorily, because sheep and cattle refuse to eat the indigestible and fibrous seed stems which it persists in throwing up; these, however, are fewer the longer it is in a pasture; crested dogstail is even worse than cocksfoot for producing "windle-straes." As regards perennial rye grass, although in meadows it dies out in spots, and is replaced by stronger growing grasses, such as cocksfoot, yet it certainly does not disappear from the pastures, even after four years, and meanwhile it has occupied the soil, kept down weeds, and furnished a greater weight of produce during the first two years than when it has been omitted. The nutritive value of rye grass was shown to be not inferior in Part I. Fream has since shown that it constitutes a large proportion of the herbage on many of our best old grass lands.

The following mixture of seeds is recommended for sowing down to permanent pasture:—Per acre, cocksfoot, 3 lb. (7½); meadow foxtail, 4 lb. (11); meadow fescue, 6 lb. (11); tall fescue, 2 lb. 12 oz. (4½); hard fescue, 1½ lb. (5½); timothy, 1½ lb. (13); perennial rye grass, 7 lb. (10); golden oat grass, ½ lb. (2½); wood meadow grass, ½ lb. (5½); smooth stalked meadow grass, 6 oz. (3½); rough stalked meadow grass, ¼ lb. (3); Dutch clover, 1½ lb. (7); alsike clover, 1½ lb. (7½); perennial red clover, 1½ lb. (2½); yarrow, 6 oz. (6). The numbers in brackets are the percentages of germinating seeds of each kind in the mixture. To obtain a mixture with these percentages, the number of seeds in 1 lb. must be known, and the germinating proportion of each, and the weight taken adjusted in accordance with this. The author has found it a good plan to sow oats after well-dunged turnips, as soon after the middle of March as possible, and to sow the grass seeds about the end of April. The oats should if possible be cut for hay towards the end of July, to give the grass seeds a good start; next spring superphosphate, kainite, and sodium nitrate should be applied as top dressing, and a hay crop taken, the grasses being cut before they are in full bloom. J. M. H. M.

The Wood of the Beech. By R. HARTIG and R. WEBER (*Bied. Centr.*, 1889, 552—555).—The original memoir (235 pp.) gives a full account of the anatomical structure, physiological functions, &c., of the beech tree. Of the whole woody tissue, cellulose forms one-half, mucilage one-fourth, and other matters one-fourth. Weber in the second half of the memoir gives ash and nitrogen analyses; the bark appears to be richest in ash, containing from 15—20 times more than the wood itself, and the ash increases with age; the percentage of ash increases from the periphery to the centre, the maximum being found in those parts where the bough twigs leave the stem, and the quantity decreases as the age nears 60 years, but after that and up to 80—90 years the ash increases and afterwards decreases.

Potash at the centre is generally double that at the periphery, but with phosphoric acid the contrary is the case, and this holds good also for sulphuric acid and magnesia. As regards nitrogen, the maximum amount is found during the first 10 years, the quantity decreasing after that time up to 60 years, again rising up to 80 years, when the second maximum is attained, and then gradually sinking.

E. W. P.

Manurial Value of several Marine Products. By A. MAYER (*Bied. Centr.*, 1889, 511—513).—The following are partial analyses of several marine products which are capable of being used as a manure:—

	Nitrogen.	Potash.	Phosph. acid.	Calc. carb. in ash.	NaCl.
	p. c.	p. c.	p. c.	p. c.	p. c.
Algæ	0·89	0·72	0·14	1·11	7·0
Mussel shells	0·08	0·11	0·10	90·8	0·05
Star-fish (*Asterias rubens*)	1·92	0·16	0·45	17·8	0·4
Egg cases of *Buccinium undatum*	3·40	0·18	0·16	4·9	5·2
Polypenstiele arturleria	3·23	0·35	0·67	19·4	4·7
Egg cases of Ray	10·56	0·48	0·40	0·9	2·2

To the seaweed it is necessary to add some cheap phosphated manure, so as to form a useful compost. Mussel shells surpass marl in value. Star-fish, owing to their brittleness and high percentage of phosphoric acid and potash, are well adapted for using alone as manure.
E. W. P.

Comparative Manurial Values of Chili Saltpetre and Ammonium Sulphate. By C. ROLLAND (*Bied. Centr.*, 1889, 508—511).—Quantities of each manure were applied to wheat, so that the weight of nitrogen in each should be equal. The results were much in favour of the nitrate, but, then as the weather had been dry and hot, it was unfavourable to obtaining the full effect from the sulphate. Besides bringing a heavier yield, the nitrate was the cheaper manure, for 200 kilos. per hectare brought a net profit of 158·5 M., whilst the ammonia only brought 34·75 M.

When increasing quantities of ammonium sulphate were compared, it was found that 50 kilos. per hectare brought a higher yield than either 100 or 150 kilos. both in straw and in grain.
E. W. P.

Analytical Chemistry.

Testing of the Reagents employed in Elementary Analysis. By M. v. NENCKI (*Monatsh.*, 10, 233—235).—The methods given by Krauch (*Die Prüfung der chemischen Reagentien auf Reinheit*) for testing the purity of copper oxide are insufficient, as commercial copper oxide frequently contains lime, an impurity which would give rise to considerable errors in analyses; a sample of the granulated substance was found to contain 0·39 per cent. and a sample of the powder 1·02 per cent. of calcium oxide. Lead chromate sometimes contains lead oxide; in one sample examined, 13·27 per cent. of lead oxide was found.
F. S. K.

Purification of Litmus. By O. Foerster (*Zeit. anal. Chem.*, **28**, 428).—The best commercial litmus is first exhausted with alcohol in the cold, then digested with water, and the solution filtered and evaporated. The residue is dissolved in water, the filtered solution precipitated by a mixture of absolute alcohol and glacial acetic acid, and the precipitate washed with alcohol; this solution, precipitation, and washing being repeated as long as any reddish-violet substance is removed thereby. The precipitate is then dried, moistening repeatedly with alcohol to remove acid. It is now dissolved in water, and the solution filtered and precipitated with feebly ammoniacal alcohol. The precipitate, once more washed with alcohol and dried, is fit for use. M. J. S.

Volumetric Apparatus. By V. Hölbling (*Zeit. anal. Chem*, **28**, 431—433).—In this arrangement, the bottle containing the standard solution serves as the base of the burette stand. The burette is supported by a rod and clip attached to a collar clamped round the neck of the bottle. Three tubes pass through the stopper of the bottle. By one of these air is forced (by a small finger pump) into the bottle to drive the solution by the second tube to the top of the burette. The third is for relieving the pressure, and is closed by a clip. The tube which conveys the solution to the burette enters at the top and passes down exactly as far as the zero point, where it is drawn off to a jet and bent to the side. It is held in its place in the burette by a cork, notched for the passage of air. The solution having been driven up into the burette until it covers the end of this tube, the relief valve is opened and the syphon action of the tube draws the solution down as far as the zero. M. J. S.

Separation of Ethereal Solutions from Aqueous Liquids. By A. Gawalovski (*Zeit. anal. Chem.*, **28**, 433—434).—In separating small quantities of ethereal or other volatile solutions from large volumes of aqueous liquids, the shaking should be performed in a flask with a very narrow neck. The flask is then inverted in a small stopcock funnel, by which the aqueous liquid is gradually run off to a second flask (where it can, if desired, be shaken a second time with ether), the volatile layer remaining in the upper flask to the last.
M. J. S.

Estimation of Iodine. By E. Reichardt and Upmeyer (*Arch. Pharm.* [3], **27**, 642—645).—Experiments were made on Duflos' method as described in Fresenius (*Quant. chem. Anal.*, 6 *Auf.*, I, 485), in which iodic acid or an iodide is heated with ferric chloride and the iodine set free is distilled over into potassium iodide solution and titrated with sodium thiosulphate solution. The authors passed the iodine directly into thiosulphate solution and determined the excess of the solution by means of permanganate. It is essential that the distilling flask should not be stoppered with cork or caoutchouc, as the iodine attacks these, and the results are then too low. A wooden stopper soaked in paraffin gave perfectly satisfactory results. A current of air is unnecessary; the whole of the iodine is carried over with the steam in a short time. J. T.

Estimation of Ammonia by Distillation. By W. M. STEIN and P. W. SCHWARZ (*Zeit. anal. Chem.*, 28, 428—431).—The apparatus used by the author completely prevents the projection of the alkaline solution into the condenser. In the cork is fitted a wide glass tube resembling a cylindrical separator bulb without the stopcock. Through the upper neck of this bulb passes the tube for connection with the condenser. It reaches nearly to the bottom of the bulb and is there narrowed and bent aside so that no drops can be thrown up into it directly. In its upper part are three side apertures for the entrance of the vapours. If these apertures are large enough, the liquid which collects in the tube is able to drain from it without any tendency to be driven forward. The drops of condensed water which form in the neck of the bulb serve to wash the vapours to some extent. The absorption vessel consists of a flask, with a side tube containing fragments of glass through which the acid is introduced; this retains the ammonia perfectly without opposing any statical resistance to the escape of air. M. J. S.

Analytical Notes. By C. DE LA HARPE and F. REVERDIN (*Bull. Soc. Chim.* [3], 1, 163—165).—To determine carbonic oxide in the atmosphere, the filtered air may be aspirated over iodic acid contained in a fractionating flask heated at 150° in an oil-bath; the carbonic oxide is oxidised to carbonic anhydride, and a corresponding amount of iodine is liberated, which the delivery tube of the flask conducts into starch solution. 9 litres of air containing 1—2/100,000 of carbonic oxide gave a very definite indication after 20 minutes.

Modification of Bunsen's apparatus for chlorine estimation.—An arrangement by which the air contained in the apparatus at starting is allowed to escape after being washed. T. G. N.

Volumetric Estimation of Sulphates. By H. QUANTIN (*Bull. Soc. Chim.* [3], 1, 21—24).—A method depending on the fact that when an alkaline sulphate is added to a hydrochloric acid solution of barium chromate, chromic acid is liberated, and this, after precipitating the excess of barium chromate by ammonia, may be titrated by a standard ferrous sulphate solution. T. G. N.

Precipitation of Magnesia. By L. BLUM (*Zeit. anal. Chem.*, 28, 452—454).—The use of sodium ammonium phosphate, instead of sodium hydrogen phosphate, for precipitation of magnesia, as proposed by Mohr, is attended with the disadvantage that in dilute solutions the precipitate forms in so finely divided a condition that it requires several days to subside completely, and if filtration is attempted before subsidence is complete, a clear filtrate cannot be obtained. For qualitative detection of magnesium, however, the ammonium salt is to be preferred. M. J. S.

Source of Error in Separating Traces of Manganese from much Lime by Ammonium Sulphide. By L. BLUM (*Zeit. anal. Chem.*, 28, 454).—From a solution containing much calcium chloride mixed with yellow ammonium sulphide and exposed to access of air, calcium thiosulphate separates in crystals on long standing. When traces of manganese are to be precipitated from such a solution, long standing is inadmissible. In such a case, it is better to boil vigorously, and, after further addition of ammonium sulphide, to filter immediately. M. J. S.

Determination of Carbon in Iron. By L. BLUM (*Zeit. anal. Chem.*, **28**, 450—452).—The author controverts the statement of De Koninck (Abstr., 1888, 1341), that the addition of silver sulphate prevents the evolution of chlorine in Ullgren's chromic combustion process, and shows by direct experiment that silver chloride when heated with the usual mixture of chromic and sulphuric acids is decomposed, with evolution of a gas absorbable by potash.
M. J. S.

Estimation of Nitrogen by Kjeldahl's Method. By F. MARTINOTTI (*Zeit. anal. Chem.*, **28**, 415—421).—The author's conclusions are as follows:—

1. For the estimation of the organic and ammoniacal nitrogen in manures in the absence of nitrates, Kjeldahl's method (use of a mixture of sulphuric acid and phosphoric anhydride with addition of mercury, and subsequent heating with permanganate) is to be preferred to that of Will and Varentrapp.
2. For the estimation of the total nitrogen where nitrates are present, Jodlbauer's modification does not give accurate results: it is better, before proceeding to Kjeldahl's process, to destroy the nitrates by heating with ferrous chloride and hydrochloric acid, and to estimate their amount separately. M. J. S.

Elementary Analysis of Volatile Liquids. By E. REICHARDT (*Arch. Pharm.* [3], **27**, 640—641).—A small glass tube sealed at one end, and capable of being closed with a cork, is half filled with copper oxide, weighed, and then charged with the volatile liquid to be burnt, and again weighed. The tube is now filled up with copper oxide, and then corked. To burn the liquid, the uncorked tube is laid on copper oxide in a platinum boat, which is placed in a combustion tube, and the combustion carried out in the ordinary way. All non-nitrogenous, volatile, carbon compounds can thus be burnt with the best results. Heavy volatile liquids which are not very deliquescent may be dropped from a small weighed vessel directly on to the copper oxide in the platinum boat; the boat is then quickly placed in the combustion tube, and the vessel is weighed a second time to determine the amount taken. J. T.

Rapid Estimation of Saccharine Compounds. By J. E. POLITIS (*J. Pharm.* [5], **20**, 62—64).—Estimation by means of Fehling's solution would be rapid if the end of the operation could be quickly ascertained. The author takes an excess of decinormal cupro-potassium solution for a measured quantity of sugar solution, and titrates the excess of copper by De Haen's method with potassium iodide and sodium thiosulphate. The decinormal cupro-potassium solution contains copper sulphate crystallised, 24·95 grams;

sodium potassium tartrate, 140 grams; sodium hydroxide, pure, 25 grams, made up to 1 litre with water; 50 c.c. of the copper solution is boiled, and 10 c.c. of sugar solution containing about 1 per 1000 of glucose is added. After boiling for five minutes, the solution is made up to 100 c.c., and 50 c.c. is filtered off. This is slightly acidified, and potassium iodide is added in excess; the iodine liberated is then titrated by means of thiosulphate. The unreduced copper is thus ascertained, the reduced copper being found by difference. 1 c.c. of the copper solution corresponds with 0·0036 gram glucose. J. T.

Estimation of Galactose. By E. STEIGER (*Zeit. anal. Chem.*, **28**, 444—450).—The amount of copper reduced from Fehling's solution by galactose is not absolutely proportional to the amount of the sugar present, but is influenced by the strength of the solution. The author, therefore, gives the following table showing the amount of copper corresponding with a given quantity of galactose under the conditions described below:—

Galactose.	Copper.	Galactose.	Copper.
250·0 mgs. gave	434·5 mgs.	125·0 mgs. gave	232·7 mgs.
237·5 „	411·8 „	112·5 „	211·1 „
225·0 „	393·6 „	100·0 „	188·7 „
212·5 „	375·0 „	87·5 „	165·4 „
200·0 „	354·2 „	75·0 „	142·4 „
187·5 „	335·0 „	62·5 „	120·2 „
175·0 „	316·4 „	50·0 „	94·8 „
162·5 „	297·6 „	37·5 „	73·1 „
150·0 „	277·5 „	25·0 „	49·9 „
137·5 „	254·0 „		

In all the experiments, the given weight of galactose was contained in 25 c.c., which was added to an excess of the boiling Fehling's solution. The latter was in all cases prepared at the time. The boiling was continued for 3 to 4 minutes, special experiments having shown that no essential difference resulted from varying the time between 3 and 7 minutes, although by boiling for 30 minutes more copper was always reduced. The precipitate was collected on an asbestos filter, and reduced by hydrogen. The Fehling's solution used each time contained 2·0784 grams of crystallised copper sulphate, 10·38 grams of potassium sodium tartrate, and 3 grams of soda in 120 c.c. M. J. S.

Discrimination of Fruit and Beet Syrups. By J. KÖNIG and M. WESENER (*Zeit. anal. Chem.*, **28**, 404—415).—The former of these preparations (Obstkraut) is the aqueous extract of apples or pears inspissated to a syrup or jelly. Owing to the difference in cost, it is frequently adulterated with beet syrup, also occasionally with starch syrup, dextrin syrup, or maltose. The most characteristic difference between the first of these and the genuine fruit syrup is their action on polarised light: in a 10 per cent. solution examined with

Laurent's polariscope, the fruit syrup gives a left-handed rotation of at least 4°, whilst beet syrup rotates the ray 5° to 7° to the right. The solution is best prepared for observation by clarifying with lead acetate. The kind of sugar present may be ascertained by the usual methods (inversion, and reduction of cupric solution); the fruit syrup is rich in dextrose (46—57° per cent.), but poor in saccharose (maximum 6·5 per cent.), whilst beet syrup contains on an average 43 per cent. of saccharose and only 18 of dextrose (maximum 23). The determination of the nitrogen (Kjeldahl's method) furnishes another means of discrimination, the fruit syrup containing at most 0·25 per cent., whilst beet syrup contains at least 0·5 per cent. The total mineral matter is on the average twice as high in beet syrup (3·8 per cent.) as in fruit syrup (1·92 per cent.). Further differences are that beet syrup exhibits stringiness, whilst fruit syrup does not, also that in a 1 per cent. solution beet syrup gives a precipitate with hydrochloric acid, which is not the case with fruit syrup; moreover, beet syrup when warmed with potash gives a disagreeable ammoniacal odour, in which trimethylamine is feebly noticeable, whilst fruit syrup gives only an agreeable fruity odour. M. J. S.

Detection of Carbamide. By E. LÜDY (*Monatsh.*, **10**, 295—316; see p. 1059).

Detection of Resorcinol. By H. BODDÉ (*Arch. Pharm.* [3], **27**, 656; from *Nederl. tijdschr. pharm. Chem. Jour.*, 1889, 163).—If some drops of sodium hypochlorite solution are added to a solution of resorcinol in water or alcohol, a violet coloration appears which soon passes into yellow. On warming, or on the addition of a considerable amount of the reagent, the liquid becomes dark yellowish-red, or dark yellowish-brown. The transient violet colour is clearly visible with 1 part of resorcinol in 10,000 parts of water, in which case the yellow colour also is persistent. Phenol, salicylic, and benzoic acids do not give the violet colour; the liquid remains colourless, or shows only a faint fluorescence; it is only after warming that it becomes slightly yellow. Further, if some drops of ammonia be first added to the resorcinol solution, sodium hypochlorite solution will produce a transient reddish-violet colour; the liquid subsequently becomes yellow, and on boiling dark green. Salicylic and benzoic acids and antifebrin are not coloured under these conditions; phenol, however, becomes greenish-blue. J. T.

Milk Analysis. By R. BOURCART (*Bull. Soc. Chim.* [3], **1**, 24—28).—An abstract of a detailed memoir deposited in the archives of the "Société Chimique de Paris." The author recommends that the density of milk should not be taken until 12—24 hours after milking, as milk does not attain its maximum degree of contraction until then. To control the sp. gr., the following formula is given:—

$$P = 1 + 0{\cdot}004(a - g) - 0{\cdot}001g,$$

P = sp. gr.; *a*, the total solids; *g*, the fat. T. G. N.

Potassium Chromate as a Reagent for the Purity of Quinine Sulphate. By J. C. de Vrij (*Chem. Centr.*, 1889, 708, from *Nieuw. tijdschr. pharm. Nederland*, 1889, 76).—2 grams of the quinine salt, dissolved in 80 c.c. of water, is treated with 0·55 gram of potassium chromate, the mixture cooled to 15°, the precipitated quinine chromate collected on a filter, and washed with small quantities of water, when the total filtrate should not exceed 80 c.c. The filtrate is rendered just alkaline with sodium hydroxide solution, when, in case much foreign alkaloïd is present, a precipitate forms. If the quantity of such alkaloïds is not more than 2 per cent., an opalescence occurs on warming the slightly alkaline filtrate to 60°. The quinine may be recovered from the chromate by dissolving in boiling water, filtering from any insoluble part, and adding it to a solution of sodium hydroxide, when the base is precipitated in a pulverulent form. The method is recommended for quantitative purposes. J. W. L.

Indirect Determination of Extractive Matters in Wine. By E. Egger (*Zeit. anal. Chem.*, **28**, 397—404).—Comparative estimations by the direct method prescribed by the German Imperial Commission of 1884, and by the indirect method of ascertaining the specific gravity after removal of the alcohol, show that the tables published by Hager (*Zeit. anal. Chem.*, **17**, 502) for the latter method almost invariably give results from 0·3 to 0·5 gram per 100 c.c. too low. The tables of Schultze (*ibid.*, **19**, 104) give much closer results, rarely differing by more than 0·3 gram per 100 c.c. from the direct estimation. The exact method of performing the direct estimation is as follows:—50 c.c. of the wine, measured at 15°, is evaporated on the water-bath in a platinum basin of 85 mm. diameter, 20 mm. height, and 75 c.c. capacity, and the residue is dried for two and a half hours in the water oven. For sweet wines, a smaller quantity, yielding from 1 to 1·5 gram of residue, is taken. According to Haas, the indirect method is applicable only to sweet wines, since in fully fermented wines the assumption on which the tables have been constructed, that the solution of the extractive matters has the same specific gravity as one of sugar, is incorrect. M. J. S.

Detection of Foreign Colouring Matter in Wine. By L. Sortegné (*Chem. Centr.*, 1889, 550, from *Staz. sperim. agr. ital.*, **16**, 13—17).—The wine to be examined is treated with $\frac{1}{10}$ volume of 10 per cent. potash, stirred for five minutes, and the liquid poured into a parchment pleated filter, which stands in water. After a few hours the yellow oxidation products of the tannin begin to pass; at the end of 24 to 48 hours, the foreign colouring matters have become fixed on the parchment, which may be judged by their colour. Natural wine merely colours the parchment yellow.

J. W. L.

Testing Logwood Extracts. By T. C. Palmer (*Chem. News*, **59**, 262).—Powdered hide is found to attract the colouring matter of logwood just as readily as it does the tannin; so the latter cannot be estimated in the logwood that way. Touching Procter's modification of Hammer's tannin process, the author states that the amount of soluble matter in hide powder depends very largely on the time the water is in contact with the hide. The watery extract from some hide powder left a variable amount of readily oxidisable residue, giving many of the reactions of the so-called coriin, which, however, when redissolved in water was precipitated on adding a solution of tannin. The latter can, therefore, not be expected to extract much coriin from the hide. D. A. L.

Estimation of Tea Tannin. By J. T. WHITE (*Chem. News*, **59**, 261—262).—Experimenting on the estimation of tannin in tea, the author found the end reaction in Lowenthal's method not quite distinct. Precipitation with excess of a standard acid solution of lead acetate, and estimating the excess of lead in the filtrate gave no results owing to the composition of the precipitate being unknown. In estimations as zinc tannate, the best results were obtained in the presence of ammonium chloride. The solution is precipitated in the cold, and allowed to remain an hour or two; the author instead of dissolving this precipitate in sulphuric acid and oxidising with permanganate, dries it at 100° and calculates the tannin from its organic matter. Zinc tannate dissolves in 14,600 parts of water at 21°, but requires 60,500 parts at 90°; it is more soluble in ammonia. Boiling tea extract with hydrated copper or aluminium oxides removes a little over one-half the extract from solution. Aluminium acetate precipitates tea tannin as long as the solution is not too acid; whereas aluminium gallate dissolves readily in acetic acid. The tannin in the aluminium precipitate, which may be easily washed, is calculated from the loss on ignition. D. A. L.

A new Reaction for Albuminoïds. By C. REICHL (*Monatsh.*, **10**, 317—320).—When two or three drops of an alcoholic solution of benzaldehyde is added to an albuminoïd, then an excess of moderately strong (1 : 1) sulphuric acid, and finally a drop of ferric sulphate, a dark-blue coloration is produced either immediately or in a short time. If the albuminoïd is solid, it first becomes blue, and the colour gradually diffuses through the liquid. This reaction is very clear with solutions containing 1 per cent. of albuminoïd, and is still visible with those containing only $\frac{1}{16}$ per cent. Salicylaldehyde and benzoic chloride give similar colorations, but not so well marked. L. T. T.

Detection of Human Blood. By S. M. COPEMAN (*Brit. Med. J.*, **2**, 1889, 190—193).—The method adopted by the author for the preparation of blood-crystals is to add serum to a drop of blood on a microscope slide; on covering this, crystals appear after a variable time. (Compare Bond, Abstr., 1888, 181.) In the case of human blood, the crystals which form consist of hæmoglobin, and are rectangular plates. In the case of monkey's blood, the crystals also consist of hæmoglobin but the plates are diamond-shaped. In the case of all the other animals whose blood was examined, the crystals invariably consisted of oxyhæmoglobin. Crystals can be obtained from bloodstains by the same method, although with greater difficulty; it is believed that by this means we have a method of distinguishing the blood of man from that of the lower animals. W. D. H.

General and Physical Chemistry.

Action of Hydrogen Chloride and Metallic Chlorides on the Photochemical Decomposition of Chlorine Water. By E. Klimenko and G. Pekatoros (*J. Russ. Chem. Soc.*, 1889, 57—65).—Bunsen and Roscoe (*Ann. phys. Chem.*, **96**, 373) have shown that hydrochloric acid has an influence on the decomposition of chlorine water by light. The authors show that not only hydrochloric acid, but also the chlorides of the following metals: K, Na, Mg, Ca, Sr, Ba, hinder the decomposition of chlorine water. Sealed tubes containing $\frac{1}{10}$ mol. weight of the hydrogen or metallic chloride and a definite amount of chlorine water of known strength were placed in sunlight, together with tubes containing the same amount of chlorine water alone. When the latter was found to be completely decomposed, the determination of the free chlorine left in the other tubes was made with decinormal thiosulphate solution. The amount of undecomposed chlorine water was found to depend—

1. On the nature of the salt in solution;
2. For one and the same salt, on the concentration; and
3. To a small extent only, on the duration of the exposure to light (14 days' action of sunlight not differing much from seven days' action). From numerous experiments, the authors conclude that by the continued action of light, chlorine water is decomposed so completely that iodine is no longer liberated by it from potassium iodide. Further, that hydrogen chloride and metallic chlorides prevent complete decomposition.

The amount of free chlorine remaining in the tubes after the decomposition of the chlorine water has proceeded as far as possible varies with different salt solutions. This residual free chlorine is considerably larger in the presence of the chlorides of the alkaline-earth metals than in the presence of those of the alkali metals, and, in every group, is found to decrease as the atomic weight of the metal increases. If the quantity of the salt added to the chlorine water is diminished to one half, then, *cæteris paribus*, the residual free chlorine is double, or more; the amount evidently depending on the strength of the chlorine water. The amount of chlorine remaining uncombined in chlorine water in presence of metallic chlorides is not affected by the time it is exposed to the action of light. B. B.

Relationships between the Composition and Absorption Spectra of Organic Compounds. By M. Althausse and G. Krüss (*Ber.*, **22**, 2065—2070; compare Krüss, Abstr., 1883, 1041; 1885, 949; 1888, 1141).—The spectra of alcoholic solutions of the hydrochlorides of thionine and dimethylthionine both show three absorption bands, one of which, namely, that nearest to the most refrangible portion of the spectrum, disappears when the solution is diluted at the moment when the other two become visible as separate bands.

The hydriodides of symmetrical dimethylthionine and diethylthionine, in alcoholic solution, give similar spectra.

The compounds formed by the hydrochlorides of tetramethylindamine sulphide and tetrethylindamine sulphide with zinc chloride give spectra with three absorption bands, one of which lies so near the red end of the visible spectrum that its wave-length cannot be measured.

Moderately dilute alcoholic solutions of thionoline and methylene violet transmit only the red rays, but on adding a considerable quantity of alcohol the blue of the spectrum becomes visible and two bands can be observed.

The two principal bands of the thionine spectrum are visible in the spectra of very dilute alcoholic solutions of the chlorides of dimethyldiethylthionine and tetrethylthionine.

Measurements of the wave-lengths of the line of maximum darkness, in the absorption bands of the compounds enumerated above, prove that, in accordance with the conclusions previously arrived at, an increase in the percentage of carbon causes the absorption bands to pass towards the less refrangible portion of the spectrum.

Measurements of the spectra of several thionine salts showed that the wave-lengths of the lines of maximum darkness are the same, whether a solution of the hydrochloride, hydriodide, or other salt is employed.

A comparison of the spectra of the compounds formed by the combination of diazobenzene chloride, or diazobenzenesulphonic acid with α-naphthylamine or α-naphthol, with those of the compounds obtained in a similar manner from tetrahydro-α-naphthylamine or tetrahydro-α-naphthol, showed that addition of hydrogen to an organic colouring matter causes the absorption bands to pass towards the blue portion of the spectrum. The spectra of the compounds examined contain no measurable absorption bands, but in all cases the field of absorption is sharply defined and permits of accurate measurement.

The relation between the composition and absorption spectrum of a compound is identical with that existing between its colour and its composition. If a substance is examined spectroscopically in a solution suitable to commercial requirements, and the rays transmitted and absorbed are accurately measured, the colour of an unknown derivative of the compound in question can be foretold with tolerable accuracy from the rules which have been found to hold good.

F. S. K.

New Apparatus for Electro-chemical Investigations. By N. v. Klobukoff (*J. pr. Chem.* [2], **40**, 121—127; compare *ibid.* [2], **39**, 412).—The author describes, with the aid of diagrams, an arrangement by which the electrolyte in quantitative electrolytic determinations can be kept in constant motion; the arrangement can be adapted to any electrolytic apparatus. F. S. K.

Electrolysis of Distilled Water. By E. Duter (*Compt. rend.*, **109**, 108—109).—Distilled water was electrolysed in an apparatus made of glass which yielded no alkali to the water even after long contact. The electromotive force was about 100 volts. Electrolysis was conducted in three different ways, namely, (1) with anode and cathode both of platinum; (2) with cathode of platinum and anode of nickel, cobalt, iron, copper, or similar metal; and (3) with anode of platinum and cathode of tin, bismuth, copper, lead, mercury, aluminium, &c.

In the first case, with a cathode consisting of a wire whilst the anode had a large surface, hydrogen alone was evolved for several days. Oxygen then appeared, but its volume was always less than half the volume of the hydrogen, and the water gradually became acid.

In the second case, the anodes were attacked and converted into hydrated protoxides, which then gradually changed to peroxides, but after very prolonged action of the current the latter were partially reduced to protoxides. This change does not take place until after several months.

In the third case, hydrogen was evolved at the cathode, whilst the metal of which it was composed gradually became oxidised. Tin, bismuth, lead, and copper cathodes were oxidised, whilst a mercury cathode became pasty at the surface and continued to evolve hydrogen for a long time after the current was interrupted. An aluminium anode is converted into the oxide, and after a time loses all coherence. It would seem that in all these cases the metal of the cathode is converted into a metallic hydride, which is decomposed by water with formation of an oxide and liberation of hydrogen. C. H. B.

Electromotive Activity of the Ions. By W. NERNST (*Zeit. physikal. Chem.*, **4**, 129—181).—Starting from the dissociation hypothesis, the author attempts to explain the causes and calculate the effects of the electromotive forces set up in electrolytes. He thus considers the potential difference between two solutions of the same electrolyte of different concentrations, between two solutions of different electrolytes, and between electrolytes at different temperatures. The conclusions arrived at from hypothesis are in each case tested as far as possible by experiment, the results obtained in most cases justifying the assumptions made. H. C.

Absolute Velocity of Ions. By C. L. WEBER (*Zeit. physikal. Chem.*, **4**, 182—188).—If N is the concentration of the solution, that is the number of milligrams of one ion contained in 1 c.c., and m is the amount of this ion deposited on one square millimeter of the electrode in one second by a current of maximum density, then the absolute velocity of the ion in question is given by m/N. By a current of maximum density is understood the maximum current which can pass through the electrolyte without giving rise to secondary reactions. The measurement of this maximum presents some practical difficulties, but the author has succeeded in determining it for solutions of one or two salts, and has thus obtained numbers for the velocity of their ions which are of the same order as those obtained by Kohlrausch. H. C.

Heat of Combination of Fluorine with Hydrogen. By BERTHELOT and MOISSAN (*Compt. rend.*, **109**, 209) :—

H gas + F gas = HF gas, develops +37·6 Cal.
H gas + F gas = HF diss., „ +49·4 „

The details of the experiments will be published subsequently. The magnitude of the thermal disturbance explains the great chemical activity of fluorine.

C. H. B.

Thermochemistry of Carboxylic Acids of the Aromatic Series. By F. STOHMANN, C. KLEBER, and H. LANGBEIN (*J. pr. Chem.* [2], **40**, 128—157).—The authors have determined the heat of combustion of a number of acids of the aromatic series; the method employed has been previously described (this vol., p. 929), and the results are given in the following table.

		Molecular weight.	Heat of combustion, Cal.	Heat of formation, Cal.
Benzoic acid	$C_7H_6O_2$	122	771·7	93·3
Orthohydroxybenzoic acid	$C_7H_6O_3$	138	729·5	135·5
Metahydroxybenzoic acid	$C_7H_6O_3$	138	729·0	136·0
Parahydroxybenzoic acid	$C_7H_6O_3$	138	725·9	139·1
Methylparahydroxybenzoic acid.	$C_8H_8O_3$	152	895·2	132·8
β-Resorcylic acid	$C_7H_6O_4$	154	676·9	188·1
Gallic acid	$C_7H_6O_5$	170	634·1	230·9
Pyrogallolcarboxylic acid	$C_7H_6O_5$	170	633·7	231·3
Orthotoluic acid	$C_8H_8O_2$	136	929·4	98·6
Metatoluic acid	$C_8H_8O_2$	136	929·1	98·9
Paratoluic acid	$C_8H_8O_2$	136	927·4	100·6
Phenylacetic acid	$C_8H_8O_2$	136	933·2	94·8
Mesitylenic acid	$C_9H_{10}O_2$	150	1085·2	105·8
β-Phenylpropionic acid	$C_9H_{10}O_2$	150	1085·5	105·5
β-Phenylacrylic acid	$C_9H_8O_2$	148	1042·3	79·7
Paraisopropylbenzoic acid	$C_{10}H_{12}O_2$	164	1238·6	115·4
α-Naphthoic acid	$C_{11}H_8O_2$	172	1232·6	77·4
β-Naphthoic acid	$C_{11}H_8O_2$	172	1228·4	81·6
Phthalic acid	$C_8H_6O_4$	166	771·6	187·4
Isophthalic acid	$C_8H_6O_4$	166	768·8	190·2
Terephthalic acid	$C_8H_6O_4$	166	770·9	188·1
Phthalic anhydride	$C_8H_4O_3$	148	784·0	106·0
Uvitic acid	$C_9H_8O_4$	180	928·9	193·1
Trimesic acid	$C_9H_6O_6$	210	767·6	285·4
Pyromellitic acid	$C_{10}H_6O_8$	254	777·4	369·6
Mellitic acid	$C_{12}H_6O_{12}$	342	788·2	546·8

It will be seen from the above table that the heat of combustion of a para-acid is slightly less than that of the corresponding ortho-compound. The heat of combustion of phenylacetic acid seems to be rather greater than that of the isomeric toluic acids, but phenylpropionic acid and mesitylenic acid have the same heat of combustion.

The heat of combustion of benzoic acid and its homologues increases about 156 Cal. in each member of the series; phthalic acid and uvitic acid show a similar difference (158·5 Cal.).

The substitution of hydroxyl for hydrogen in benzoic acid increases the heat of combustion 43·6 Cal.; the heat of combustion of dihydroxybenzoic acid is 51·2 Cal. more than that of hydroxybenzoic acid, but when hydroxyl is substituted for a third hydrogen atom, the increase is only 43 Cal.

A table is given showing that the effect of displacing hydrogen by carboxyl in phenols and hydrocarbons of the aromatic series is to decrease the heat of combustion by about 4·8 Cal.

A comparison of the heat of combustion of acetic and propionic acids with that of phenylacetic and phenylpropionic acids shows that the substitution of hydrogen for phenyl increases the heat of combustion 722·5 and 721·2 Cal. respectively; the difference in the case of formic and benzoic acids is about 715 Cal.

The difference (12·4 Cal.) between the heat of combustion of phthalic acid and its anhydride is practically the same as that between benzoic acid and its anhydride and between acetic acid and its anhydride. F. S. K.

Thermochemistry of Acids of the Oxalic Series and of Fumaric and Maleic Acids. By F. Stohmann, C. Kleber, and H. Langbein (*J. pr. Chem.* [2], **40**, 202—229).—In this paper the authors give details of the determination of the following thermal values by burning the substances in a bomb at a pressure of 24 atmospheres:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Oxalic acid, $C_2H_2O_4$	60·2	196·8
Malonic acid, $C_3H_4O_4$	207·3	212·7
Succinic acid, $C_4H_6O_4$	356·8	226·2
Methylmalonic acid, $C_4H_6O_4$	364 8	218·2
Glutaric acid, $C_5H_8O_4$	517·2	228·8
Dimethylmalonic acid, $C_5H_8O_4$	515·3	230·7
Ethylmalonic acid, $C_5H_8O_4$	517·9	228·1
Methylsuccinic acid, $C_5H_8O_4$	515·2	230·8
Adipic acid, $C_6H_{10}O_4$	668·9	240·1
Methylethylmalonic acid, $C_6H_{10}O_4$	672·3	236·7
Propylmalonic acid, $C_6H_{10}O_4$	675·0	234·0
Isopropylmalonic acid, $C_6H_{10}O_4$	675·2	233·8
Symmetrical dimethylsuccinic acid, $C_6H_{10}O_4$	671·0	238·0
Unsymmetrical dimethylsuccinic acid, $C_6H_{10}O_4$	671·7	237·3
Ethylsuccinic acid, $C_6H_{10}O_4$	672·2	236·8
Methylglutaric acid, $C_6H_{10}O_4$	670·8	238·2
Pimelic acid, $C_7H_{12}O_4$	829·6	242·4
Suberic acid, $C_8H_{14}O_4$	985·6	249·4
Azelaic acid, $C_9H_{16}O_4$	1141·3	256·7
Sebacic acid, $C_{10}H_{18}O_4$	1296·8	264·2
Fumaric acid, $C_4H_4O_4$	320·1	193·9
Maleic acid, $C_4H_4O_4$	326·3	187·7

The authors compare their results with those of other observers, and conclude with some remarks as to the relations existing between the thermal values of the isomerides and homologues in the above list.

A. G. B.

Heat of Dissolution of Anhydrous Lithium Bromide. By A. Bodisco (*J. Russ. Chem. Soc.*, 1889, **21**, 7—9).—Crystals of the hydrated bromide $LiBr,H_2O$ were dehydrated on heating them in a current of hydrogen at 300°. The determination was made in the same way as in the case of lithium iodide (this vol., p. 329) and yielded the number 11,351 cal. A comparison of the values obtained by the author with those obtained by Thomsen for the chloride affords another proof of the validity of Beketoff's principle that the energy of a chemical reaction depends on the magnitude of the combining chemical masses.

	Heat of formation.	Heat of dissolution.	Heat of formation in aq. solutions.
LiCl	93,810	8,440	102,250
LiBr	79,959	11,351	91,310
LiI	61,214	14,886	76,100

B. B.

Thermochemistry of the Nitrocamphors and Cyanocamphor. By Berthelot and P. Petit (*Compt. rend.*, **109**, 92—95).—The molecular heat of combustion of α-nitrocamphor is 1370·5 Cals. at constant volume and 1371·4 Cals. at constant pressure, hence its heat of formation from its elements is +89·1 Cals. The action of nitric acid on camphor with production of the α-derivative develops +7·3 Cals. This number is of the same order as the heat developed in the formation of ethyl nitrite (+6·2) and nitroglycerol (4·7 × 3), and hence it would seem that α-nitrocamphor should have explosive properties. In fact, if this compound is dropped into a glass tube previously heated to redness, or if its vapour is superheated, it detonates. When treated with sodium hydroxide at 23°, +7·46 Cals. is liberated, and this quantity is the heat of neutralisation, less the heat of dissolution, the latter being unknown.

β-Nitrocamphor forms a hydrate with 1 mol. H_2O, and the molecular heat of combustion of this compound is 1332·8 Cals. at constant volume and 1334·3 Cals. at constant pressure; hence its heat of formation is +195·2. The heat of dissolution of the hydrate is −2·76 Cals., and of the anhydrous compound −1·80 Cals.; it follows that the heat of hydration is +0·96 Cal., the molecular heat of combustion of the anhydrous compound is 1333·8 Cals. at constant volume and 1335·3 Cals. at constant pressure, and its heat of formation +125·2 Cals. The action of nitric acid on camphor, with formation of the β-derivative, develops +43·4 Cals., a number of the same order of magnitude as the corresponding values for nitro-derivatives of the benzene series. It follows that the difference between α- and β-nitrocamphors is of the same order as that between an alkyl nitrite and a nitro-derivative. The β-derivative is not explosive. When treated with sodium hydroxide, the development of heat, +12·7 Cals., is similar to that which accompanies the formation of benzoates, &c.

A further quantity of alkali produces no further thermal disturbance, and hence β-nitrocamphor is a strong acid and resembles trinitrophenol in this respect.

Cyanocamphor has a molecular heat of combustion of +1494·8 Cals. at constant pressure and 1496·3 Cals. at constant volume; its heat of formation is +58·5. When treated with excess of sodium hydroxide, −1·24 Cals. is absorbed. This quantity is the difference between the heat of neutralisation and the heat of dissolution, and it is evident that the former is but small. C. H. B.

Thermochemistry of Phenylenediamines. By L. VIGNON (*Compt. rend.*, **109**, 477—479; compare Abstr., 1888, 1012).—Metaphenylenediamine was prepared in the usual manner, and the heats of dissolution and neutralisation were determined directly. Heat of dissolution −3·2 Cals; heats of neutralisation as follows:—

	Hydrochloric.	Sulphuric.	Acetic.	Oxalic.
First equivalent....	+7·0	+8·3	+4·4	+6·6
Second equivalent ..	+11·7	+14·2	+6·0	+8·6

Orthophenylenediamine was obtained by the reduction of orthonitraniline; it crystallises in white lamellæ which melt at 71°. Solution in water and acids is too slow to permit of direct determination in the calorimeter. If hydrogen chloride is passed into an ethereal solution of the diamine, white crystals of the composition $C_6H_4(NH_2)_2$, 3HCl, $5H_2O$, separate, and this compound was used in the determinations. Heat of dissolution −8·2; heats of neutralisation by three successive equivalents of potassium hydroxide +12·2, +10·6, +7·0 respectively. The heats of neutralisation of the three phenylenediamines by hydrochloric acid are as follows:—

	Ortho.	Meta.	Para.
First equivalent........	7·0	7·0	8·8
Second equivalent......	10·1	11·7	14·7

These results are similar to those obtained by Berthelot and Werner with the dihydric phenols and hydroxybenzoic acids; the heat of neutralisation is greatest for the para- and least for the orthoderivative (Abstr., 1885, 628 and 1032). C. H. B.

Electrolytic Dissociation versus Hydration. By S. ARRHENIUS (*Phil. Mag.* [5], **28**, 30—38).—Objections have been raised by Mendeléeff and others to the theory of electrolytic dissociation on the ground that the assumption of the existence of hydrates in solution serves to explain all the facts on which this theory is founded. Questions which Mendeléef has put forward as to the influence of temperature and concentration on the isotonic coefficients *i* of Van't Hoff and de Vries have been already answered by the author; and in this paper evidence which has been advanced in support of the hydrate theory is criticised.

The following table is given of those branches of physical science which have received an explanation from the hypotheses of osmotic pressure and electrolytic dissociation.

Group A.—1. Osmotic pressure. 2. Lowering of freezing point. 3. Lowering of vapour-pressure. 4. Raising of boiling point. 5. E.M.F. of concentration currents in solutions.

Group B.—6. Conductivity of electrolytes.

Group C.—7. Diffusion of electrolytic solutions.

Group D.—8. Change of the degree of dissociation of weak acids with dilution. 9. Conductivity of mixed solutions. 10. Change of strength of weak bases and acids by the addition of neutral salts. 11. Distribution of bases amongst different acids (Thomsen's avidity).

Group E.—12. Velocity of reactions of various chemical processes caused by the presence of acids and bases.

Group F.—Additive properties of electrolytic solutions, such as:—13. Specific volume and specific gravity. 14. Heat of neutralisation. 15. Compressibility. 16. Internal friction. 17. Colour, rotatory power, and index of refraction.

Of the above, many of the phenomena belonging to Groups B, C, and F are directly opposed to the assumption of hydrates in solution. For instance, if such a substance as potassium chloride exists in solution as the hydrate KCl,mH_2O, then its ions will be K,nH_2O and $Cl,(m-n)H_2O$, and since the velocity of an ion is smaller the more atoms it contains, the velocity of the potassium ion must be greater the smaller the value of n. Kohlrausch has, however, shown that the potassium ion travels at the same rate in solutions of all the potassium salts, and, therefore, would have to be always combined with the same amount of water. But as we have no ground for attributing any particular value to n, and as it is besides probable that many salts (most of those of potassium, for example) exist only in the anhydrous state, the simplest and likeliest assumption is that the ions of the salts, and, consequently, the salts themselves, exist in solution without water of hydration.

The occurrence of singular points, such as maxima, minima, points of inflexion, angular points, on the curves obtained when any property of a solution is plotted against the percentage of dissolved substance has been taken as indicating the presence of hydrates. In this way, Graham came to the conclusion, from the fact that the internal friction of solutions of alcohol in water had a maximum near 36 per cent. alcohol, that probably a hydrate, $C_2H_5\cdot OH,5H_2O$, exists in solution—a conclusion which was abandoned when it was found that the maximum varies with the temperature. In fact it is obvious that in any not too simple curve singular points will occur, and that, if we look in this way for evidence of the existence of hydrates, we shall certainly find it—for every property can be represented by a curve which is usually not very simple.

Mendeléeff seeks to deduce the existence and composition of hydrates from the curves which represent the first derived functions of the specific gravity as a function of the percentage composition by weight (Abstr., 1888, 343). The fact, however, that the values of the first derived functions can be represented by straight lines would mean nothing more than that the values of the specific gravity s as a function of the percentage composition p can be represented by a certain number of interpolation formulæ of the second degree with three times the number of arbitrary constants. Five such formulæ with 15 constants—of which Mendeléeff only uses 10—are employed in the case of sulphuric acid. Mathematically, this only implies that the analytical representation cannot be considered satisfactory, and that, with a little trouble, a much better representation could probably be found. This would possibly result if the specific gravity were plotted against molecular instead of percentage composition.

The results obtained by Pickering (Proc., 1889, 89) are open to the same criticism in a yet greater degree. Pickering differs from Mendeléeff as to the rectilineal nature of the first derived function, but finds that the second derived function, d^2s/dp^2, consists of straight lines, there being, in the case of sulphuric acid, 17 such straight lines corresponding with 16 hydrates. That is, the specific gravity can be represented in the form of 17 equations of the third degree, with 68 arbitrary constants. With such a number of constants, the points at which breaks are supposed to occur, and which should correspond to definite hydrates, can practically be chosen arbitrarily. This is evidenced by the fact that, although Pickering agrees in general with the conclusions arrived at by Crompton by a similar examination of the electrical conductivity, he differs from him in some of the details as to where breaks occur. H. C.

The Nature of Solutions. By S. U. PICKERING (*Phil. Mag.* [5], **28**, 148).—The author states that Arrhenius will find his objections already answered in his (the writer's) paper whenever it is published. S. U. P.

Determination of the Specific Gravity of Soluble Salts. By J. W. RETGERS (*Zeit. physikal. Chem.*, **4**, 189—205).—The specific gravity of a soluble salt can be determined by the method already described by the author (this vol., p. 812), even when greater than that of the liquid employed, if a crystal of the salt be attached to a glass float. This float is made of thin rod, bent into horse-shoe form, so that the crystal can be inserted and held firm between the extremities. If p is the weight of the float, and p' that of the salt, s the specific gravity of the float, and S that of float and salt combined, then the specific gravity of the salt σ is given by $S/\{1-p/p'(S/s-1)\}$. The best results are obtained when p is made as small and p' as large as possible.

The following numbers were obtained by the above method :—

	Sp. gr.		Sp. gr.
$Pb(NO_3)_2$	4·531	$AgNO_3$	4·352
$BaBr_2,2H_2O$ ..	3·827	$AgClO_3$	4·401

The temperature in each case is about 20°. H. C.

Dilatation of Salt Solutions. By N. A. TCHERNAY (*J. Russ. Chem. Soc.*, 1889, **21**, 73—77).—In continuing his researches (compare this vol., p. 204), the author has studied the dilatation by heat of the following nitrate solutions, the results being given as before for the volumes:—

(1) $HNO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0001595t + 0{\cdot}000003699t^2$
(2) $LiNO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0001471t + 0{\cdot}000003673t^2$
(3) $(NH_4)NO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0001534t + 0{\cdot}000003590t^2$
(4) $NaNO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0002144t + 0{\cdot}000003194t^2$
(5) $KNO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0001746t + 0{\cdot}000003575t^2$
(6) $AgNO_3 + 50H_2O \; v_t = 1 + 0{\cdot}0001593t + 0{\cdot}000003587t^2$
(7) $Mg(NO_3)_2 + 100H_2O \; v_t = 1 + 0{\cdot}0001552t + 0{\cdot}000003483t^2$
(8) $Ca(NO_3)_2 + 100H_2O \; v_t = 1 + 0{\cdot}0001719t + 0{\cdot}000003531t^2$
(9) $Sr(NO_3)_2 + 100H_2O \; v_t = 1 + 0{\cdot}0001787t + 0{\cdot}000003557t^2$

and the dilatation coefficients for—

(1) $\delta = 0{\cdot}0001595 + 0{\cdot}000007399t$
(2) $\delta = 0{\cdot}0001471 + 0{\cdot}000007346t$
(3) $\delta = 0{\cdot}0001534 + 0{\cdot}000007180t$
(4) $\delta = 0{\cdot}0002144 + 0{\cdot}000006388t$
(5) $\delta = 0{\cdot}0001746 + 0{\cdot}000007149t$
(6) $\delta = 0{\cdot}0001593 + 0{\cdot}000007173t$
(7) $\delta = 0{\cdot}0001552 + 0{\cdot}000006966t$
(8) $\delta = 0{\cdot}0001719 + 0{\cdot}000007063t$
(9) $\delta = 0{\cdot}0001787 + 0{\cdot}000007114t$

The above dilatation coefficients are very nearly equal, the greatest discrepancy being shown by sodium nitrate. The same is the case as regards the alteration of the dilatation coefficients with rise of temperature, the increase being nearly equal to 0·0000071 for every degree. These values approach each other most closely at 40°. The metallic radicle has a much smaller influence on the different values than the acid radicle or than the relation of the number of salt molecules to that of the water molecules. The change of volume by heat corresponds with the dissociation of the hydrates in solution, so that the number of the salt hydrates in solution and their constitution is very nearly the same for solutions of 1 mol. of a salt of a univalent metal in 50 mols. of water and 1 mol. of a salt of a bivalent metal in 100 mols. of water. This fact is best explained by assuming that nitric acid in solution exists at least as a double molecule $(HNO_3)_2$.

B. B.

Contraction of Solutions. By CHARPY (*Compt. rend.*, **109**, 299—301).—The author adopts Gouy and Chaperon's definition of the coefficient of contraction, namely, the rate at which the volume of the solvent varies as it penetrates the solution; it is calculated by means of the formula $K = \frac{D_0}{D}(1 + \frac{S}{D}\frac{dD}{dS})$, S being the weight of salt contained in 100 parts of the solution of sp. gr. D. This coefficient is always less than unity, varies with each solution, and decreases continually as the concentration of the solution increases. Adopting Raoult's method, the results are represented by curves the abscissæ of which are the values of $1 - K$, and the ordinates the values of

$\frac{1-K}{P}$, P being the weight of salt in 100 parts of the solvent. All the curves have the same general form, and consist of a curvilinear portion indicating that whilst the solution is dilute the value of $1-K$ rapidly increases, and a rectilinear portion which corresponds with a higher degree of concentration, and is either parallel with or inclined to the axis of the abscissæ.

When the curve is parallel with the axis of the abscissæ, the contraction is proportional to the weight of salt dissolved in a given weight of the solvent, a result which is obtained with most anhydrous salts, such as sodium and ammonium chlorides, strontium nitrate, and also with acetic acid. In the last two cases, the character of the curve indicates that the condition of the dissolved substance does not vary as the concentration of the solution increases, a result which does not agree with the supposition made by Raoult to explain the anomalous cryoscopic behaviour of these compounds.

The cases in which the rectilinear part of the curve is inclined to the axis of the abscissæ may be explained by supposing that the dissolved salts exist in solution in the form of hydrates, and that the contraction is proportional to the weight of the hydrate dissolved in a given quantity of the solvent.

If the equivalents of dissolved substances are multiplied by the respective values of $\frac{1-K}{P}$, which corresponds with the point of intersection of the axes of the ordinates and the prolongation of the rectilinear portion of the curve, the numbers obtained are approximately constant in a series of analogous compounds.

Ammonium chloride	0·01445	Ferrous sulphate	0·0651
Potassium chloride	0·01412	Zinc sulphate	0·0674
Sodium chloride	0·01404	Manganese sulphate	0·0572
Lithium chloride	0·01312		
		Potassium sulphate	0·0261
Acetic acid	0·0131	Sodium sulphate	0·0293
Formic acid	0·0128	Potassium carbonate	0·0292

C. H. B.

Rate of Change in the Inversion of Cane Sugar by Acids. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **4**, 226—248).—The influence of temperature on the rate of change, ρ, is best expressed by an equation of the form $\rho t_1 = \rho t_0 \cdot e^{A(T_1 - T_0)/T_0T_1}$, where ρt_1 and ρt_0 are the rates of change for the temperatures t_1 and t_0, A is a constant, and T_0T_1 are the temperatures on the absolute scale. The above equation, which is found to be in good agreement with the experimental results, is in theoretical accordance with the assumption that during the inversion the whole of the cane sugar present does not take part in the reaction, but only a certain "active" portion, an assumption also in agreement with the results of other observations on the inversion of cane sugar. Thus the influence of neutral salts in increasing the rate of change is assumed to be due to an increase in the amount of the "active" cane sugar caused by the addition of these salts. This influence is only very slight for substances which are not dissociated (non-electrolytes), but is very marked in the case of a dissociated substance. It is to be inferred from the latter fact that the ions of the acid which effects the inversion will also have some influence on the amount of "active" cane sugar, and on this and the above assumptions the rates of inversion for various cases are calculated, and the numbers obtained found to agree with those observed. The amount of "active" cane sugar is, however, not wholly conditioned by the acid, and hence the want of proportionality between the rate of inversion and the amount of dissociation. On the other hand, since the action of a dissociated substance is practically that of its ions, the influence of such a substance should be an additive property as far as the ions are concerned, and this, by comparison of the effects of the nitrates and chlorides of sodium, potassium, and ammonium, and the chlorides, bromides, and nitrates of hydrogen and potassium, appears to be the case. It likewise appears that the influence of the ions both of the acids and neutral salts is independent of the temperature. H. C.

Estimation of the Coefficients of Affinity of Organic Bases and Acids. By E. LELLMANN (*Ber.*, **22**, 2101—2103).—Certain organic dyes are known to undergo change of colour in the presence of acids, others in the presence of alkalis, and the author has made use of this property as a means of determining the coefficients of affinity of organic bases and acids, the extent of the change being estimated by a spectro-photometric method. Dimethylamidoazobenzene dissolved in 25 per cent. alcohol gives a yellow solution which allows all green rays to pass through, but on the addition of a small quantity of hydrochloric acid it changes in colour to an intense red, giving at the same time a broad absorption-band in the green. This yellow solution can be employed to determine the coefficients of affinity of organic bases, and the method consists in introducing the hydrochlorides of the bases in molecular proportion into equal volumes of the solution, and noting in each case the change of colour produced, a slight change of colour indicating a strong base, and *vice versâ*. As determined in this way, aniline, β-naphthylamine, and α-naphthylamine are found to diminish in basicity in the order named. With acids, a solution of phenolphthaleïn can be employed to determine the coefficients of affinity; thus, when molecular proportions of sodium salicylate, phenol, sodium metahydroxybenzoate, and sodium parahydroxybenzoate are dissolved in equal quantities of water, and equal amounts of phenolphthaleïn are added to each solution, together with some very dilute caustic soda solution, the change of colour to red takes place in the order named, whence the author concludes that the influence of the COONa radicle on the OH group in the three hydroxy-acids is least in the ortho- and greatest in the para-compound. W. P. W.

Atomic Weights of the Elements. By DELAUNEY (*Compt. rend.*, **109**, 526—527).—When the elements are arranged in the order of their atomic weights, each atomic weight differs from that immediately preceding it by the square root of a whole number. This number is variable, but is always harmonic, that is, contains as primary factors only the numbers 1, 2, 3, and 5. C. H. B.

Determination of Molecular Weights of Polymeric Compounds by Raoult's Method. By R. MELDOLA and F. W. STREATFEILD (*Chem. News*, **60**, 66—67).—Experiments were made to ascertain the possibility of determining the molecular weight of polymeric compounds by the Raoult method. Aldehyde in benzene gave high results, 55, 54, 57, owing, it is presumed, to its containing polymerides; paraldehyde in water gave irregular results, owing, it is suggested, to the action of the solvent, inasmuch as it (paraldehyde) gave good results in benzene and acetic acid. Metaldehyde in acetic acid gave abnormal results, 72·6, very probably due to interference of solvent. From the results, it would seem possible to determine the molecular weights of some polymeric compounds by this method; the authors have, however, evidence of its failure in some cases with certain polymeric diazoamido-compounds. Benzene is the most convenient solvent. Success or failure of the method in the case of polymerides is without doubt determined by the stability of the molecule of the substance in the solvent. D. A. L.

Inorganic Chemistry.

Liberation of Chlorine during the Decomposition of Chlorates. By W. SPRING and E. PROST (*Bull. Soc. Chim.* [3], 1, 340—343)—The amount of chlorine liberated when potassium, sodium, barium, aluminium, silver, copper, zinc, lead, and mercuric chlorates are heated under varying conditions has been estimated. The nature of the chlorate has considerable influence on the quantity of chlorine set free, the latter varying from 0·02 per cent. with potassium chlorate to 14·45 per cent. with the zinc salt. Rapid heating considerably augments the percentage, as does the presence of free carbonic, silicic, or phosphoric anhydrides. In the case of potassium chlorate, the admixture with phosphoric anhydride determines an increment in the free chlorine of 55 per cent. The authors conclude that chlorates decompose according to the equations—

$$(1)\ 2MClO_3 = M_2O + Cl_2O_5;$$
$$(2)\ Cl_2O_5 = Cl_2 + O_5;$$
$$(3)\ M_2O + Cl_2 = 2MCl + O.$$

This last reaction is incomplete when by rapid heating the chlorine is removed from the sphere of action, or when the presence of silica or phosphoric anhydride hinders its union with the base. This tendency to decompose under the influence of heat into an acid and basic group gives the old dualistic formulæ some significance. T. G. N.

Autoxidation. By F. Hoppe-Seyler (*Ber.*, **22**, 2215—2220).—A reply to Traube (this vol., p. 937).

Sulphites. By P. J. Hartog (*Compt. rend.*, **109**, 179—182, 221—223, and 436—439).—Normal potassium sulphite is obtained by dissolving 100 grams of potassium hydroxide in 200 c.c. of water free from oxygen, saturating with sulphurous anhydride, and then adding a further quantity of 100 grams of potassium hydroxide dissolved in as little water as possible. The solution is evaporated in a vacuum, and the crystals are drained on cotton wool in an atmosphere of nitrogen. Since the salt is less soluble in hot water than in cold, it is advisable to keep the funnel warm when collecting the crystals. The sulphite is thus obtained in small, anhydrous, hexagonal prisms with basal modifications. It is deliquescent, but oxidises less rapidly than its solution; heat of dissolution —1·75 Cal.

Normal sodium sulphite is obtained in the same way in anhydrous crystals of the same form, always mixed, however, with a certain proportion of the heptahydrated salt; heat of dissolution + 2·71.

Sodium potassium sulphite, $NaKSO_3$, is obtained in crystals, which resemble those of the simple anhydrous salts, by adding potassium hydroxide to sodium anhydrosulphite. When the solution of the double sulphite has been partially oxidised, and is then gradually concentrated, the crystals which separate are first heptahydrated sodium sulphite, then the double sulphite, and lastly potassium sulphate; hence it would seem that at first the potassium sulphite alone undergoes oxidation. Heat of dissolution of the double salt —1·19 Cal.; heat of dissolution of hydrated sodium sulphite in a solution of potassium sulphite —11·01 Cal.; heat of formation of the double sulphite +3·76 Cal.

When a solution containing potassium and ammonium sulphites in equivalent proportions is concentrated, the first crystals consist solely of potassium anhydrosulphite. These are followed by monohydrated ammonium sulphite, in which part of the base is replaced by potassium. In presence of a large excess of ammonia, hexagonal prisms of the composition $1{\cdot}14(NH_4)_2O,0{\cdot}86K_2O,2SO_2$ are obtained, together with acicular crystals of the composition $K_2O,10(NH_4)_2O,$[illegible]$SO_2 + 11H_2O$. This salt dissociates at the ordinary temperature, and [illegible] it is enclosed in a sealed tube containing nitrogen, ammonium sulphite condenses in the upper part of the tube.

No sodium ammonium sulphite could be obtained.

The double sulphite, $2Na_2O,K_2O,4SO_2+9H_2O$, is obtained by saturating two molecular proportions of sodium carbonate with sulphurous anhydride, adding one molecular proportion of potassium carbonate and concentrating. It separates in rounded crystals which cannot be dehydrated without decomposition. At 90° the salt undergoes no change, and at 100—110° it loses water and sulphurous anhydride. Heat of dissolution, —30·39 Cal.; heat developed by the action of potassium oxide on two molecular proportions of sodium anhydrosulphite, +16·81 Cal.; heat of formation of the double salt, +25·88 Cal.

The salt $2Na_2O,(NH_4)_2O,4SO_2 + 9H_2O$ always separates from mixtures of sodium and ammonium sulphites. It can readily be obtained in a crystalline form by passing ammonia gas into a saturated solution of sodium hydrogen sulphite. Its heat of dissolution is −30·72 Cal. The action of ammonia on sodium anhydrosulphite develops +15·68 Cal.; the formation of the solid salt from $2Na_2SO_3$ sol + $(NH_4)_2S_2O_5$ sol + $9H_2O$ sol, therefore, develops +19·62 Cal.

An analogous potassium compound also exists.

The reaction $2Na_2S_2O_5 + (NH_4)_2O$ develops + 15·68 Cal. if the solution of the sodium salt is freshly prepared, but only 12·94 Cal. if the solution has been kept in an atmosphere of nitrogen for three months. The author distinguishes the two modifications as α- and β-, and it is evident that the conversion of the former into the latter develops +2·74 Cal. The action of ammonia on the double salt just described develops +23·52 Cal. if it has been prepared from anhydrosulphite α; +23·87 Cal., if from anhydrosulphite β; and +23·87 Cal. if from Marignac's salt.

Berthelot has shown (*Ann. Chim. Phys.* [6], **3**, 242), that a solution which contains 2 mols. of sulphurous anhydride and 1 mol. of potassium oxide alters spontaneously with development of +2·6 Cal., 2 mols. of potassium hydrogen sulphite forming 1 mol. of the anhydrosulphite with elimination of water. According to de Forcrand, no similar change occurs with the sodium salt, but the fact that a similar thermal disturbance is observed seems to point to the opposite conclusion.

The action of two successive molecules of ammonium oxide on the two molecules of potassium anhydrosulphite develops +25·05 Cal. and 23·32 Cal. respectively, the corresponding values for the α-sodium salt being 26·16 Cal., and 23·52 Cal., and for the β-salt 23·42 Cal. and 23·87 Cal. respectively. The fact that the heat of neutralisation of the fourth acid function by ammonia is less than the heat of neutralisation of the first three, indicates that the anhydrosulphites contain four equivalents of metal in the molecule. With sodium or potassium hydroxide in place of ammonia, however, the four heats of neutralisation are identical. Nevertheless the author considers that this view is supported by the existence of double sulphites such as $3MgO,Am_2O,4SO_2 + 18H_2O$ and $3CdO,Na_2O,4SO_2$. C. H. B.

Behaviour of Sodium Thiosulphate with Acids and Metallic Salts. By G. VORTMANN (*Ber.*, **22**, 2307—2312).—The author takes exception to the views put forward by Vaubel with reference to the decomposition of sodium thiosulphate by acids (this vol., p. 943), and points out that the experimental method adopted (treatment of sodium thiosulphate in a large flask with acids of different degrees of concentration, at one time in the cold, at another on heating, but always in such a way that the products remained in contact for some hours, and then were diluted with water previous to the determination of the decomposition products) is one extremely favourable to the occurrence of secondary reactions. To avoid as far as possible the formation of secondary products, the author experimented thus: the aqueous solution of the thiosulphate was heated to the boiling point with either more or less than the theoretical quantity of the dilute acid or solution of the metallic salt in a small flask, through which a slow stream of either carbonic anhydride or hydrogen was passed from the commencement of the experiment, in order to remove the sulphurous anhydride formed in the reaction, and prevent its oxidation in the vessel by the oxygen of the air; the contents of the flask were then examined for the other products of the decomposition. As a result, the author finds that the initial decomposition of thiosulphuric acid is expressed by the equation: $2H_2S_2O_3 = 2H_2S + O_2 + 2SO_2$; the end-products varying with the nature of the acid or metallic salt present. In those cases in which metals are present which do not form insoluble sulphides, the oxygen partially oxidises the hydrogen sulphide with the separation of sulphur, and the sulphurous anhydride is set free, whilst in those cases in which the metal present yields a sulphide insoluble in dilute acids, a precipitate of the sulphide is formed, and the oxygen reacts either with the sulphurous anhydride with the formation of sulphuric acid, or with a portion of the undecomposed sodium thiosulphate with the production of tetrathionate or pentathionate; the last reaction, however, ensues only in those cases in which either an excess of thiosulphate is present, or the metallic salt undergoes reduction from a higher to a lower state of oxidation.

With dilute hydrochloric acid, sodium thiosulphate reacts according to the equation, $Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2 + H_2O$. When dilute solutions of the thiosulphate are employed, a small quantity of hydrogen sulphide escapes, but with concentrated solutions no noticeable amount is obtained, since the small quantity evolved is decomposed by the sulphurous anhydride with the separation of sulphur, which collects on the sides of the flask above the liquid. In addition to the sulphur and sulphurous anhydride, tetrathionic acid is formed in quantity corresponding with that obtainable from 20 per cent. of the thiosulphate employed, and traces of pentathionic acid are present, but no evidence could be obtained of the presence of sulphuric acid in the decomposition product. The formation of pentathionic acid is not mentioned in Vaubel's paper. The reaction is slightly modified when certain salts of the alkalis or alkaline earths are present; thus, in the presence of potassium iodide, the quantity of liberated sulphur is increased and small amounts of sulphuric acid are formed.

On treatment with aluminium chloride, sodium thiosulphate reacts according to the equation $Al_2Cl_6 + 3Na_2S_2O_3 + 3H_2O = Al_2(OH)_6 + 6NaCl + 3S + 3SO_2$. Tetrathionic acid is formed in quantity corresponding with that obtainable from about 4 per cent. of the thiosulphate employed, and at the commencement of the reaction a small quantity of hydrogen sulphide escapes, but no trace of sulphuric acid could be detected. Addition of potassium iodide at the commencement of the experiment brings about the formation of sulphuric acid in this case also.

The results obtained by the action of sodium thiosulphate on copper sulphate have already been communicated (Abstr., 1888, 787); the amount of sulphuric acid formed corresponds so well with that required by the equation there given that the method can be employed volumetrically for the estimation of copper.

Mercury salts react with sodium thiosulphate with the formation of the metallic sulphide, and the filtrate contains sulphuric acid in large quantity together with traces of tetrathionic acid, but no pentathionic acid.

In the presence of a sufficient excess of sodium thiosulphate, arsenious acid is completely converted into the sulphide, and the filtrate contains chiefly tetrathionic acid, together with traces of pentathionic acid. With arsenious acid in excess, however, the reaction is expressed by the equation $As_2O_3 + 9H_2S_2O_3 = As_2S_3 + 3H_2S_4O_6 + 3SO_2 + 6H_2O$. Arsenic acid and sodium thiosulphate yield arsenious sulphide, together with much pentathionic acid and traces of sulphuric acid.

The action of sodium thiosulphate on antimonious chloride corresponds with that on arsenious acid; the filtrate from the antimonious sulphide contains only traces of sulphuric acid, but much tetrathionic acid.

When sodium thiosulphate is boiled with a faintly acid solution of stannous chloride, tin sulphide and hydroxide are precipitated and the filtrate contains sulphuric and pentathionic acids. If, however, the solution is strongly acid, the tin remains in solution, sulphuric and polythionic acids are formed, and much sulphur is liberated, probably owing to the reduction of the sulphurous anhydride by stannous chloride. Stannic chloride yields similar results: tin sulphide and hydroxide are precipitated and the filtrate contains sulphuric and polythionic acids. W. P. W.

Solidification of Nitrous Anhydride. By F. Birhans (*Compt. rend.*, **109**, 63).—Oxygen and nitric oxide, dried by passing over pumice moistened with sulphuric acid and then over baryta and calcium oxide, and strongly cooled, were allowed to mix in a receiver cooled to −54° by the rapid evaporation of methyl chloride. One volume of oxygen was mixed with six to eight volumes of nitric oxide, in order to avoid the formation of nitrogen peroxide. A beautiful blue liquid was at once formed, which could only be solidified by means of a mixture of methyl chloride and solidified carbonic anhydride. According to Cailletet and Colardeau, the temperature of this mixture is −82°. C. H. B.

Conditions of Action of Nitric Acid. By C. F. Cross and E. J. Bevan (*Chem. News*, **60**, 13—14).—The authors have observed that by eliminating the intervention of nitrous acid, by the employment of carbamide, the activity of nitric acid may be greatly reduced or even almost arrested. A sample of dilute nitric acid nearly reduced ligno-cellulose (jute) to cellulose in seven hours, but by adding increasing quantitites of carbamide nitrate to the same acid, its activity was gradually diminished, until ultimately scarcely any action on the jute fibre could be observed under otherwise similar conditions. In the same way, 50 c.c. of nitric acid (1·05 sp. gr.) dissolved 4·465 grams of copper in four hours, but the same acid under the same conditions, but in the presence of carbamide, only dissolved 0·020 gram of copper. The production of nitrocelluloses by the action of a mixture of nitric and sulphuric acids is not impeded by adding carbamide; this may be regarded as further evidence that these compounds are alcoholic nitrates. It is pointed out that nitrogenous organic substances, such as aniline and carbamide, which generally resist the action of chromic acid mixture, oxidise readily when a small quantity of potassium nitrate is also added. D. A. L.

Solubility of Carbonic Anhydride in Chloroform. By Woukoloff (*Compt. rend.*, **109**, 61—63).—A known volume of carbonic anhydride was brought in contact with a large volume of chloroform which had previously been carefully freed from air. When solution was complete, the pressure and volume of the gas and vapour were measured, the readings being repeated after 24 hours, and again after 48 hours. A second quantity of the gas was now introduced, and the same set of observations was made. The addition of successive volumes of gas was repeated many times, and the results, which are given in the form of a table, are calculated on the assumption (1) that carbonic anhydride strictly obeys Boyle's law; (2) that the pressure of the mixed gas and vapour is exactly the sum of the partial pressures; and (3) that the change in the volume of the chloroform in consequence of the solution of the gas is so small that it may be neglected.

The results show that the volume of gas dissolved is slightly greater than that required by Dalton's law, although the differences are very small. A similar result has previously been obtained with carbon bisulphide. It follows that there is a distinct connection between the compressibility of carbonic anhydride alone and when in contact with chloroform. C. H. B.

Constitution of Potassium Polysulphides. By W. Spring and J. Demarteau (*Bull. Soc. Chim.* [3], **1**, 311—315).—From the following experimental data, the authors consider that polysulphides are not to be regarded as sulphites or sulphates in which oxygen is replaced by sulphur, but as resulting from the solution of sulphur in potassium monosulphide.

1. The strength of potassium monosulphide solutions has little influence on the amount of sulphur dissolved after the formation of a compound, $K_2S_{4\cdot48}$, and the quantity of sulphur dissolved is not appreciably affected by temperature until the formation of this compound, after which it is a function of the temperature according to the equation—

$$S_t = S_0 (1 + 0\cdot000956t + 0\cdot00000193t^2),$$

S_0 = sulphur dissolved or combined with the potassium at 0°;
S_t = " " " " t°.

2. Iodine is supposed to form polysulphides from monosulphides by uniting with the metallic element from each of two monosulphide molecules, whose residues thereupon combine, as—

$$KS{\cdot}SK;\ KS_2{\cdot}S_2K;\ KS_3{\cdot}S_3K,\ \&c.,$$

If, however, a solution of potassium sulphide be added to a solution of iodine in potassium iodide in such proportions as should form the sulphides K_2S_2, K_2S_3, &c., much sulphur is always liberated, which dissolves if the possible polysulphide is not higher than K_2S_4, but otherwise is precipitated. Iodine does not therefore determine the synthesis of polysulphides.

3. Potassium sulphite and potassium polysulphide solutions of varying concentrations, when mixed in equivalent proportions at different temperatures react, yielding in each instance potassium monosulphide and potassium thiosulphate; the action appears to proceed with equal facility and at the same rate in both these cases :—

$$K_2S_2 + K_2SO_3 = K_2S + K_2S_2O_3;\text{ and}$$
$$K_2S_4 + 3K_2SO_3 = K_2S + 3K_2S_2O_3.$$

4. All potassium polysulphides are reduced to the monosulphide when their solutions are shaken with mercury, according to the equation—

$$K_2S,Sx + x\mathrm{Hg} = x\mathrm{HgS} + K_2S.$$

5. Solutions of potassium polysulphides dialyse without decomposition.

6. Potassium polysulphides react with ethyl iodide and bromide to form ethyl bisulphide, which dissolves the sulphur set free; there is no production of ethyl monosulphide; in this case the polysulphides appear to be solutions of sulphur in potassium bisulphide. Ethyl tetrasulphide reacts with potassium sulphite, to form ethyl bisulphide and potassium thiosulphate. T. G. N.

Cistern Deposits. By A. S. Chapman (*Chem. News*, **60**, 56).—The author has analysed three deposits taken from a copper cistern, in which water had been softened by the Clark process. In two cases the material was very hard and stony, and the lime found in excess of that present as carbonate bore a relation to the silica corresponding nearly with that required by a salt of the composition $2CaSiO_3,3CaO$ (probably as a hydrated compound with 4 mols. H_2O). The third sample was softer, and, besides copper and carbonic anhydride, contained also much silica and arsenic. D. A. L.

Zinc and Cadmium Chromites. By G. Viard (*Compt. rend.*, **109**, 142—144).—A boat containing normal potassium chromate is placed in a porcelain tube, and behind it is placed a similar boat containing zinc chloride. The tube is heated to a somewhat high temperature, and a slow current of hydrogen or carbonic anhydride is passed through it, so that the vapour of the chloride is carried over the chromate. After the tube is cooled, the boat which contained the chromate is found to contain a black, crystalline mass, consisting of zinc chromite mixed with some zinc oxide and unaltered potassium chromate. After treatment with water and boiling hydrochloric acid, the chromite ZnO,Cr_2O_3 is obtained in brilliant, black, regular, microscopic octahedra with a greenish lustre; sp. gr. at 15° = 5·29, and the hardness is greater than that of quartz. The chromite is not attacked by acids, but is decomposed by fused potassium hydroxide and nitrate.

Cadmium chromite, CdO,Cr_2O_3, may be obtained in a similar manner, but the yield is small, probably owing to the formation of cadmium chromate, which is more stable than zinc chromate. The chromite forms small black aggregations of octahedra, harder than glass, but not so hard as quartz; sp. gr. at 17° = 5·79.

The specific volume of cadmium chromite is 24·2; of manganese chromite 23; of zinc chromite, 22·1; and of magnesium chromite, 21·9. C. H. B.

Cupric Oxybromide Analogous to Atacamite. By E. BRUN (*Compt. rend.*, **109**, 66—68).—If a warm saturated solution of cuprous chloride in a solution of sodium, potassium, or ammonium chloride is exposed to the air, it gradually deposits a crystalline powder of the same composition as atacamite. In like manner, a solution of cuprous bromide in a solution of potassium bromide yields a precipitate which, after being washed with a solution of potassium bromide, consists of small, distinct, deep green, quadratic crystals of the composition $CuBr_2,3CuO,3H_2O$. They are insoluble in water, but dissolve easily in dilute acids, and in ammonia. At 180—190° they remain practically unaltered; at 210—215° they become anhydrous, but a small quantity of cupric bromide is volatilised; at 240—250° decomposition takes place, and if the residue is treated with water, cupric bromide dissolves, and a residue of cupric oxide is left undissolved. If the cuprous bromide solution is mixed with hydrogen peroxide, the oxybromide is precipitated immediately, but is amorphous. When an excess of a concentrated solution of potassium bromide is added to a solution of cuprammonium sulphate at 100°, the same oxybromide is obtained as a green, crystalline precipitate.
C. H. B.

Oriental Enamel on Tiles and its Imitation. By J. BOECK (*J. pr. Chem.* [2], **40**, 158—171).—The author has analysed a Turkish blue enamel taken from a mosque built by Timur, with the following percentage results:—

SiO_2.	CuO.	PbO.	CaO.	MgO.	SnO_2.	K_2O.	Na_2O.	$Fe_2O_3 + Al_2O_3$.
53·53	3·51	17·90	3·00	0·33	6·86	3·51	7·27	3·11

and traces of arsenic and manganese.

The earthenware from which the enamel was taken has the percentage composition SiO_2, 60·35; Al_2O_3 and Fe_2O_3, 18·10; CaO, 14·52; MgO, 3·72; and CO_2, 2·68.

An enamel to all appearances identical with the above can be prepared as follows:—A mixture of sand (53·53 parts), copper oxide (3·51 parts), litharge (18·3 parts), chalk (5·4 parts), tin oxide (6·9 parts), potassium carbonate (5·2 parts), and sodium carbonate (12·5 parts) is heated in a Hessian crucible until the mixture softens just sufficiently to form a glass without dissolving the oxide of tin; it is then poured into water, powdered, moistened with water, and burnt on to the clay. As the lead and copper oxide are reduced in a muffle, the burning must be carried out in a Hessian crucible in a wind furnace. The earthenware employed was made from a marly clay, and was moderately hard-burnt, but very porous. F. S. K.

Molecular Weight of Aluminium Chloride. By L. F. NILSON and O. PETTERSSON (*Zeit. physikal. Chem.*, **4**, 206—225).—The authors have redetermined the vapour density of aluminium chloride, using both the V. Meyer and the Dumas methods. Their conclusions are that aluminium chloride only attains the condition of a perfect gas above 800°, and that below this temperature it is in a continually dissociating state. When the above temperature is reached the density of the vapour corresponds with the formula $AlCl_3$, and this remains practically unaltered at the highest attainable temperature (1600°). From this behaviour of the chloride it follows that aluminium is undoubtedly a trivalent element.

With regard to the methods used, the authors only agree with Friedel and Craft's criticism of the V. Meyer method (Abstr., 1888, 1040) when applied to a dissociating vapour. As soon as the vapour density becomes constant they hold that with proper precautions both methods are equally accurate. H. C.

Reaction between Solutions of Ferric Chloride and Potassium Iodide. By D. J. CARNEGIE (*Chem. News*, **60**, 87—90).—The decomposition of acid solutions of potassium iodide appears to be a function of time and temperature; it can be arrested by surrounding them with an inert atmosphere, except when the solutions are strong and the temperature high.

The author has made numerous experiments with solutions of potassium iodide and ferric chloride of known strengths, and although many of his results indicate that a ratio of 1 mol. of KI to 1 atom of Fe is sufficient to effect the decomposition, yet, by taking into consideration the conditions of the experiment and the various secondary reactions, he considers that the equation:—$FeCl_3 + 3KI = FeI_2 + I + 3KCl$, is more probably the correct representation of the reaction than the equation:—$FeCl_3 + KI = FeCl_2 + KCl + I$. For the volumetric estimation of ferric iron, the ratio Fe to liberated iodine is alone considered, and is the same in both equations. The distillation method is considered preferable to the digestion process. The solution of potassium iodide is placed in the flask, saturated with carbonic anhydride, the ferric solution added, and distillation proceeded with as rapidly as possible; the volatilised iodine being caught in potassium iodide solution saturated with carbonic anhydride (to neutralise any hydroxide present). For the distillation, it is convenient to have the delivery-tube ground into the neck of the flask, so as to permit of speedy detachment; for the delivery of the thiosulphate the author employs an improvised "stillimeter," on the principle of Mariotte's bottle. The "after-blueing" of the starch sometimes observed in the titration is considered as due to the sodium iodide formed during the titration, reinforcing the small residue of potassium iodide, which in its turn reacts on the residual ferric chloride, establishing a fresh equilibrium, until some more thiosulphate is added, when the same reactions take place again, until all the ferric chloride is destroyed.

It is pointed out that commercial potassium iodide nearly invariably contains sufficient free potash to vitiate in some degree all iodometric estimations effected with its aid. The potassium iodide solution used to absorb the iodine liberated in such estimations should be supersaturated with carbonic anhydride previous to use.

D. A. L.

Passivity of Cobalt. By E. SAINT-EDME (*Compt. rend.*, **109**, 304—305).—Pure cobalt is instantly attacked by concentrated nitric acid, and if the metal is withdrawn, exposed to air, and again immersed, the action is as vigorous as before. Contact with steel or nickel does not, as in the case of iron, arrest the action of the acid. Cobalt is, however, not attacked by dilute nitric acid in the cold.

Electrolytic cobalt, unlike electrolytic iron or nickel, does not contain nitrogen, and yields no ammonia when heated in pure hydrogen. After being heated in pure nitrogen for a long time at a bright red heat, cobalt is somewhat less rapidly attacked by nitric acid, a fact which points to the possible existence of a passive nitride of cobalt, similar to the passive nitrides of nickel and iron. The passivity of the three metals follows the order of their attraction for nitrogen, which is, nickel, iron, cobalt.

C. H. B.

Cobalt and Nickel. By G. KRÜSS and F. W. SCHMIDT (*Ber.*, **22**, 2026—2028; compare this vol., p. 349).—Nickel which has been most carefully purified by the best methods known, still contains traces of foreign substances, especially iron, manganese, and magnesium, but by frequently repeating the processes the metal can be obtained free from all known elements.

The metal thus purified is invariably separated into two portions, when it is treated with ammonium sulphide, as previously described, and especially when it is fractionally precipitated as basic nickel ammonium arsenite. Of these two parts, the one has always a lower (56—58), the other a higher (61—100), atomic weight than that which, up to the present time, has been considered to be the atomic weight of nickel.

The same results were obtained with the metal purified by Zimmermann for his atomic weight determinations.

The above atomic weight values were obtained by reducing the respective oxides with pure hydrogen.

The metals obtained by reducing the oxides employed for the atomic weight determinations were subsequently submitted to a careful qualitative analysis. It was found that the metal of lower atomic weight contained no known element, the presence of which would lower the atomic weight of a metal such as nickel, and that the metal of higher atomic weight contained no known element the presence of which would give results higher than 58·6.

These results confirm the authors' views on the compound nature of nickel; analogous investigations with pure cobalt are in progress.

F. S. K.

Crystallised Cobalt and Nickel Hydroxides. By A. DE SCHULTEN (*Compt. rend.*, **109**, 266—268).—10 grams of cobaltous chloride, $CoCl_2 + 6H_2O$, is dissolved in 60 c.c. of water, and heated with 250 grams of potassium hydroxide. After solution is complete the vessel is allowed to remain for 24 hours, and, if necessary, is agitated in order to promote the separation of crystals. The cobaltous hydroxide separates as a deep violet powder which, under the microscope, is seen to consist of brownish-red, elongated, rhombic prisms, grouped in bundles. Sp. gr. at 15° = 3·597. They are pleochroic and are rose-coloured along n_g, rose-yellow along n_m, and pale brownish-yellow along n_p. They are not altered by contact with air, and are insoluble in ammonia and a cold solution of ammonium chloride, but are dissolved by acetic acid and by a hot solution of ammonium chloride. Cobalt hydroxide is also soluble in sodium hydroxide.

Ferrous hydroxide is obtained in a similar manner with 5 grams of anhydrous ferrous chloride, 130 grams of water, and 200 grams of sodium hydroxide. It forms very small, green, flattened prisms, which, even after they have been washed with alcohol and ether and dried out of contact with air, oxidise immediately they are brought into the atmosphere, with considerable development of heat and formation of ferric oxide.

Nickelous hydroxide is quite insoluble, even in the strongest solutions of potassium or sodium hydroxide. C. H. B.

Barium Cobaltite: Existence of a Cobalt Dioxide with Acidic Properties. By G. Rousseau (*Compt. rend.*, **109**, 64—66).—15 grams of hydrated barium chloride or bromide are mixed with 5 to 6 grams of finely-powdered barium oxide, and gradually heated just to redness in an open platinum crucible. When the mixture is fused, 1 gram of cobalt sesquioxide is added in successive small portions, and the heating is continued.

When a bunsen flame is used, each addition of the cobalt oxide is followed by an energetic evolution of oxygen, but the mixture soon enters into quiet fusion, and a crust of barium cobaltite quickly forms at the surface. After cooling, the product is washed with hot water, and finally with acetic acid. Brilliant, black, hexagonal lamellæ are thus obtained; they have the composition $BaO,2CoO_2$, and dissolve in concentrated hydrochloric acid with evolution of chlorine. The quantity of crystals formed, at first increases, but afterwards diminishes owing to decomposition which is accompanied by slow evolution of oxygen. After prolonged heating, crystals of cobalt oxide are obtained, which are free from barium. If, however, the superficial layer of crystals is continually pressed down into the fused mass beneath, the proportion of barium oxide in the product increases, and the composition of the crystals approximates to BaO,CoO_2.

At a higher temperature, the product consists of large, iridescent, black prisms, which approximate very closely to the composition BaO,CoO_2, but always contain a small proportion of barium platinate as an impurity. They dissolve in cold hydrochloric acid with evolution of chlorine, and in nitric acid with effervescence. The crystals decompose at a temperature somewhat higher than that at which they are formed, and at an orange-red heat decomposition is very rapid.

The temperature of formation of the normal cobaltite seems in fact to lie between 1000° and 1100°. A somewhat similar phenomenon has already been observed in the case of barium and strontium manganites, but in these instances the normal manganite was formed at the lower temperature, and the acid manganite at a higher temperature.

It follows from these experiments that cobalt can form a dioxide which, like manganese dioxide, has acidic properties. C. H. B.

Ammonio-cobaltic Molybdate, Tungstate, and Vanadate: Separation of Cobalt and Nickel. By A. CARNOT (*Compt. rend.*, **109**, 109—112).—If a solution of a cobalt salt is converted into a purpureo-cobaltic salt by the action of hydrogen peroxide in presence of ammonium chloride and ammonia, and is then mixed with ammonium molybdate, there is no change, but on the addition of excess of acetic acid, a bulky, rose-coloured precipitate is formed. This retains its colour after being washed and dried, but when heated it becomes violet, then dark-green, and afterwards yellowish-green, the colour changes corresponding with the successive evolution of water, ammonia, and oxygen. The residue consists of cobaltous molybdate, but if heated above redness it is partially decomposed into crystallised cobaltous oxide and crystallised molybdic anhydride. The dried hydrated salt has the composition $Co_2O_3,10NH_3,7MoO_3,3H_2O$, and the product after heating to redness has the composition $2CoO,7MoO_3$.

Cobaltous and nickel salts are not precipitated by ammonium molybdate from either an acid or an ammoniacal solution, but a crystalline deposit of a double ammonium cobalt or ammonium nickel molybdate may form slowly if the solution is neutral and highly concentrated. Hence the formation of the purpureo-molybdate may be used for the detection and separation of purpureo-salts in presence of cobaltous salts and for the separation of cobalt from nickel.

The solution is made alkaline with ammonia, mixed with hydrogen peroxide, heated until evolution of oxygen ceases, cooled, diluted if necessary, and then mixed with acetic acid in such quantity that the liquid contains from 3 to 5 per cent. of the free acid. Ammonium molybdate is then added until precipitation is complete, and the precipitate is washed with water containing a small quantity of ammonium chloride, and dried. The filter-paper is separated as completely as possible, and burnt by itself; the precipitate is heated to dull redness, but not beyond. The weight of precipitate multiplied by 0·1332 gives the weight of cobaltous oxide which it contains, whilst the factor 0·1048 gives the quantity of metallic cobalt. This method gives good results, both qualitatively and quantitatively, and it may be applied in presence of copper and zinc. In order to make the separation more exact, the moist precipitate is redissolved in ammonia, and reprecipitated with acetic acid, a little more ammonium molybdate being added.

The nickel in the filtrate is precipitated by boiling with sodium hydroxide until all ammonia is expelled, and after being filtered off and washed, the nickel hydroxide is dissolved in nitric or hydrochloric acid, and precipitated with sodium hydroxide and bromine. The nickelic oxide thus obtained is quite free from molybdenum.

C. H. B.

Purpureo-cobaltic Tungstate and Vanadate. By A. CARNOT (*Compt. rend.*, **109**, 147—149).—If ammonium tungstate is added to a solution of a purpureo-cobaltic salt acidified with acetic acid, a bulky rose-coloured precipitate is formed, similar to that given by ammonium molybdate, under the same conditions (preceding abstract). At 100° it becomes lilac, and if still further heated dull-blue, then dark-green, and finally pale yellowish-green, losing successively water, ammonia, and oxygen. At a bright-red heat it is stable and infusible, and after cooling has a bluish-grey colour. The composition of the hydrated precipitate is $Co_2O_3,10NH_3,10WO_3 + 9H_2O$, and after ignition $CoO,5WO_3$.

As cobaltous and nickel salts give no precipitate under the same conditions, the tungstate, like the molybdate, might be used for the separation of these salts from cobaltic salts. The composition of the precipitate, however, is not quite constant, and the ammonium tungstate itself is comparatively insoluble. There is also a greater tendency to form a crystalline nickel cobalt tungstate.

In ammoniacal solution, the purpureo-cobaltic salts give the same precipitate as in presence of an acid; cobaltous salts give a precipitate of the composition $15WO_3,2CoO,8(NH_4)_2O,3H_2O$, which alters easily on exposure to air, and has a rose colour when dried; nickel salts gives a bluish precipitate, which forms slowly, and is often accompanied by acicular crystals of ammonium tungstate.

Ammonium vanadate when added to a purpureo-cobaltic solution containing free acetic acid gives an orange-red precipitate of the composition $Co_2O_3,10NH_3,5V_2O_5 + 9H_2O$, which when heated to dull-redness agglomerates and intumesces, the colour changing to dark-grey, and afterwards to reddish-brown. Above a dull-red heat, it melts completely, and becomes black; after cooling it has the composition $2CoO,5V_2O_5$. Cobaltous and nickel salts are very slowly precipitated by ammonium vanadate in an acid solution, but in presence of excess of ammonia they give an immediate precipitate. Cobaltous salts yield green cobaltous vanadate, which alters rapidly on exposure to air, and becomes yellow; at 100° it becomes reddish-brown, and after fusion has the composition $CoO,2V_2O_5$. Nickel salts yield an orange-yellow precipitate which becomes brown at 100°, and after fusion is black and has the composition NiO,V_2O_5. The same nickel vanadate is obtained by adding excess of ammonia to the original acetic acid solution. The normal vanadate is formed, but with greater difficulty, in presence of a large excess of ammonia. Nickel salts, however, give no precipitate with a colourless neutral or slightly ammoniacal solution of ammonium vanadate. C. H. B.

Chromium. By E. JÄGER and G. KRÜSS (*Ber.*, **22**, 2028—2054).—*Ammonium chromates.*—In preparing ammonium chromate by various methods, even when a large excess of ammonia is employed, no compound is formed containing a larger proportion of ammonia than the normal salt does, and the existence of the compound $5(NH_4)_2O,4CrO_3$, described by Pohl (*Wien. Akad. Ber.*, **6**, 592), cannot be confirmed.

Ammonium chromate has not hitherto been obtained pure by any of the known methods of preparation. When an aqueous solution of chromic acid is evaporated with ammonia, the salt is partially decomposed with evolution of ammonia, and a mixture of chromate and dichromate is always obtained; even when the solution is evaporated at 50—60°, reddish-yellow crystals containing 59·19 per cent. of chromic oxide are obtained, and at ordinary temperatures, also, a mixture of the two salts is produced.

Pure ammonium chromate can be prepared by treating chromic acid, free from sulphuric acid, with ammonia of sp. gr. 0·9, adding ammonia and warming gently until the solid salt which separates is redissolved, and then placing the solution in a freezing mixture. It crystallises in long, golden needles, of the monosymmetric system; $a : b : c = 1·9603 : 1 : 2·4452$; $\beta = 64° 47'$; observed faces ∞P̶∞, OP, + P̶∞, ∞P. Perhaps, like potassium chromate, it exists in two distinct physical modifications. Its specific gravity is 1·886 at 11°. When an aqueous solution of this salt is repeatedly evaporated it is first converted into the dichromate, and eventually brown chromic oxide separates from the solution. It is not particularly stable in the dry state, and on exposure to the air it gradually turns reddish-yellow, owing to the formation of the dichromate; it also decomposes in a dry atmosphere or when gently heated.

Ammonium trichromate, prepared by Siewert's method (*Zeitsch. gesammt. Naturwiss.*, **19**, 22), always contains small quantities of the nitrate, even after having been repeatedly pressed on porous plates, and heated at 100°. The salt can be obtained free from nitrate by dissolving ammonium dichromate in a hot concentrated solution of chromic acid; the solution is concentrated, allowed to cool, and the bright-red crystals pressed and dried at 100°. The sp. gr. of the salt prepared by the aid of nitric acid is 2·329 at 10°; that obtained by crystallisation from chromic acid is 2·342 at 13°. It turns dark-brown at 160—170° (compare Siewert, *loc. cit.*), and at 190° it explodes violently, with evolution of nitrogen dioxide, leaving a residue of greenish-black chromic oxide. It is not deliquescent, and is only slowly decomposed on exposure to moist air, but it is immediately converted into the dichromate and chromic acid by water.

The salt obtained by Darmstädter (this Journ., 1871, 199) by treating a dichromate with nitric acid is neither a nitrodichromate nor a nitrotrichromate as he supposed, nor is ammonium tetrachromate formed in this way, as stated by Wyrouboff (Abstr., 1881, 352); when ammonium dichromate is dissolved in nitric acid of sp. gr. 1·41, ammonium trichromate is obtained.

Ammonium tetrachromate, $(NH_4)_2Cr_4O_{13}$, separates in crystalline crusts when ammonium trichromate is dissolved in warm nitric acid of sp. gr. 1·09, and the solution allowed to cool slowly; the product is almost pure, and contains only traces of nitric acid. It is less stable than the other salts, and deliquesces on exposure to moist air, being partially converted into chromic acid and the dichromate. Its sp. gr. is 2·343 at 10°. It turns black at 160°, melts at 170°, and decomposes suddenly at 175°, with evolution of nitric oxide, leaving a residue of dark-green chromic oxide.

When ammonium trichromate is crystallised from very concentrated nitric acid, deliquescent, amorphous precipitates are obtained, which, judging from the results of analyses, are probably mixtures of higher chromates. One sample gave 72·85 per cent. of chromic oxide which agrees approximately with the formula $(NH_4)_2O,11CrO_3$. Analyses of several products obtained from ammonium trichromate and the very strongest nitric acid gave results from which the existence of a penta-, hexa-, or higher chromate cannot be inferred with certainty. Attempts to prepare the salt (hexachromate) described by Rammelsburg (*Ann. Phys. Chem.*, **94**, 516) were unsuccessful, and only resulted in the formation of ammonium chromate.

Chromates of Potassium.—Potassium trichromate can be prepared in a pure state by treating the dichromate with nitric acid of sp. gr. 1·19; the potassium nitrate separates almost immediately when acid of this concentration is employed, and if the clear liquid is then decanted, the trichromate crystallises from the solution in red, monoclinic prisms. The specific gravity of the salt thus obtained is 2·648 at 11°. The pure salt can also be prepared by Hauer's method (*Wien. Akad. Ber.*, **39**, 439), but more quickly by dissolving the dichromate in a hot, concentrated aqueous solution of chromic acid; on cooling a considerable quantity of the trichromate, the sp. gr. of which is 2·667 at 10°, crystallises from the solution in monoclinic prisms. It is quickly decomposed by water into chromic acid and the dichromate, and it cannot be recrystallised from this solvent, as stated by Bothe (*J. pr. Chem.*, **46**, 184); it is not deliquescent, but on continued exposure to the air it gradually becomes darker in colour. It turns black at 220°, and melts at 250°; not at 140—150°, as stated by Bothe (*loc. cit.*).

Potassium tetrachromate is best prepared by dissolving the dichromate in hot concentrated nitric acid of sp. gr. 1·41; it can also be obtained by crystallising the trichromate from a hot concentrated solution of chromic acid. It forms small, probably rhombic, plates, and is not deliquescent, as stated by Siewert. It gradually darkens on exposure to the air, melts, and turns black at 215°, and is decomposed by water, but it crystallises unchanged from nitric acid of sp. gr. 1·41. Its specific gravity is 2·649 at 11°.

The analyses of the potassium chromates referred to above were carried out as follows:—The salt is reduced with hydrochloric acid, and the chromium, after precipitation with ammonia, is estimated in the usual manner. A fresh portion of the salt is dissolved in a little water, reduced with sulphurous anhydride, and evaporated with a slight excess of the reducing agent in a platinum crucible. The double sulphate, or sulphite, obtained is then ignited for a short time, and completely converted into potassium sulphate and chromic oxide; the difference between the combined weight of these compounds and that of the chromic oxide, which has been already estimated, gives the quantity of potassium sulphate. If the chromic oxide has not been previously determined, the potassium sulphate is extracted with water and the residual oxide is ignited and weighed.

This method can be conveniently employed for the estimation of a fixed alkali in presence of oxides such as alumina, ferric oxide, chromic oxide, &c.; the results are more accurate than those obtained by the methods usually employed.

Double Salts of Chromates with Mercuric Chloride.—The salt $(NH_4)_2Cr_2O_7,HgCl_2$ separates in red, well-defined, anhydrous prisms when a solution of mercuric chloride (1 part) and ammonium dichromate (1 part) is evaporated until crystallisation commences and it is then allowed to cool (compare Richmond and Abel, this Journal, 1850, 199). When double the quantity of ammonium dichromate is employed, the result is the same; but, if double the quantity of mercuric chloride is used, the excess of this salt separates first and the double salt afterwards. It is partially decomposed by water, and it cannot be recrystallised from a solution of mercuric chloride, but it separates unchanged from a cold, saturated solution of ammonium dichromate. Its sp. gr. is 3·109 at 13°.

The *salt* $3(NH_4)_2Cr_2O_7,HgCl_2$ cannot be obtained from the mother-liquors from the preceding compound, as stated by Richmond and Abel (*loc. cit.*), but it can be easily prepared by mixing solutions of ammonium chromate (1 part) and mercuric chloride (1 part), separating the precipitate which is produced and treating it with hydrochloric acid exactly sufficient for complete solution. The solution is then acidified with a few drops of hydrochloric acid and evaporated until crystallisation commences; the double salt separates on cooling in reddish-yellow needles of sp. gr. 2·158 at 10°.

The *compound* $4(NH_4)_2Cr_2O_7,HgCl_2$ can be obtained by mixing a solution of ammonium chromate (1 part) with a solution of mercuric chloride (1 part), dissolving the precipitate in exactly twice as much hydrochloric acid as is necessary for complete solution, and evaporating until crystals begin to separate. It can also be prepared by dissolving the salt $(NH_4)_2Cr_2O_7,3HgCl_2$ in a concentrated solution of ammonium chromate with addition of fuming hydrochloric acid. It forms reddish-yellow crystals.

The *salt* $(NH_4)_2Cr_2O_7,3HgCl_2$ separates in reddish-yellow needles when a solution of ammonium chromate (2 parts) and mercuric chloride (3 parts) is treated with hydrochloric acid in such quantity that the precipitate which forms is just redissolved, and the mixture then evaporated.

The salt $(NH_4)_2Cr_2O_7,4HgCl_2$ crystallises from the mother-liquors from the preceding compound in long, reddish-yellow needles.

The salt $K_2Cr_2O_7,HgCl_2$ can be prepared in a pure state by evaporating a solution of potassium dichromate (1 mol.) with mercuric chloride (1 mol.) under reduced pressure at the ordinary temperature; it forms reddish-yellow crystals of sp. gr. 3·531 at 11°, and crystallises unchanged from water.

Mercurammonium chloride mercurichromate, $2NH_2HgCl,HgCrO_4$, separates as a yellow precipitate when a solution of ammonium chromate (1 part) is added to a solution of mercuric chloride; it is readily soluble in hydrochloric acid and nitric acid, and it is gradually decomposed by water.

An orange-yellow, *basic mercuric chromate*, $5HgO,CrO_3$, is formed when the preceding compound is boiled with water; it is only sparingly soluble in warm nitric acid, but it dissolves freely in hydrochloric acid, giving a salt which is gradually reconverted into the basic chromate by boiling water.

A bright yellow *compound*, $6HgO,CrO_3$, is obtained when the preceding compound is repeatedly boiled with fresh quantities of water.

Silver Chromates.—Silver dichromate cannot be employed for determining the atomic weight of chromium, as it always contains small quantities of the chromate.

Pure silver chromate can be prepared only by repeatedly boiling the dichromate with fresh quantities of water until no further solvent action occurs. The salt thus prepared is deep-green in colour, and is completely insoluble in water, and is only sparingly soluble in nitric acid, sulphuric acid, and ammonia. The compound obtained by treating silver chromate with ammonia crystallises in long, yellow, tetragonal needles, and has the composition assigned to it by Mitscherlich, namely, $Ag_2CrO_4,4NH_3$.

The purest commercial chromium always contains chromic oxide and considerable quantities of silica. The pure metal can be obtained by reducing chromic chloride with pure zinc (compare Wöhler, *Annalen*, **111**, 230), the portions in proximity to the sides of the crucible being neglected. It crystallises in tin-white rhombohedra, and is soluble in acids, except concentrated nitric acid, which has no action even at its boiling point.

Specific heat determinations made with Bunsen's ice calorimeter in the manner previously described (Krüss and Wilson, *Zeit. physikal. Chem.*, **1**, 391) gave 0·12162 at temperatures between 0° and 98·24° as the average of two experiments; the atomic heat is, therefore, normal and equal to 6·36.
F. S. K.

Phosphotungstic Acid. By E. PÉCHARD (*Compt. rend.*, **109**, 301—304).—Mixtures of metatungstic and phosphoric acids in proper proportions were concentrated in a dry vacuum and afterwards in dry air. The acid $P_2O_5,24WO_3 + 59H_2O$ crystallises in small, colourless or yellowish, highly efflorescent rhombohedra, which closely resemble cubo-octohedra. According to Sprengel, this acid contains 61 mols. H_2O, and, according to Gibbs, only 53 mols. H_2O, but these differences are doubtless due to the highly efflorescent character of the crystals.

The acid $P_2O_5,20WO_3 + 62H_2O$ crystallises in very efflorescent, regular octohedra, and if these are dissolved in a small quantity of water and the solution concentrated, less efflorescent rhombohedra are obtained of the composition $P_2O_5,20WO_3 + 50H_2O$.

The acid $P_2O_5,16WO_3 + 69H_2O$ crystallises in colourless, regular, octohedra; and the acid $P_2O_5,12WO_3 + 42H_2O$, which is the most easily prepared of all, separates in large, monoclinic prisms.

From the method of preparation, it would seem that metatungstic, and not orthotungstic, acid combines with phosphoric acid. The phosphotungstates of sodium and barium can be obtained by the union of the corresponding orthophosphates with metatungstic acid.
C. H. B.

Action of Water on Stannic Chloride. By L. VIGNON (*Compt. rend.*, **109**, 372—375).—The author has previously shown (this vol.,

p. 833) that the changes in an aqueous solution of stannic chloride are connected with variations in the function of the stannic acid; the liquid, in fact, may be regarded as consisting of water, hydrochloric acid, and stannic acid, the latter undergoing gradual polymerisation, which is limited by the presence of the hydrochloric acid. The action of potassium hydroxide on the stannic chloride solution shows that SnO_3H_2 diss. + 4HCl diss. + Aq develops only 3·4 Cal., a number so low that complete separation of the stannic acid and hydrochloric acid is very probable, especially in dilute solution. The polymerisation of the stannic acid is indicated by the gradual decrease in the heat of neutralisation (*loc. cit.*). A freshly prepared dilute solution of stannic chloride remains clear when mixed with excess of potassium hydroxide, but if the addition is not made until several hours after the preparation of the solution, a precipitate of potassium polystannates is formed. After remaining for some days without any addition of alkali, the solution deposits opalescent polystannic oxide.

Polymerisation is accelerated by dilution and by rise of temperature, but is retarded by hydrochloric acid and alkaline chlorides. If metastannic acid is heated, with a large excess of potassium chloride solution, in sealed tubes at 150° the heat of neutralisation of the metastannic acid increases considerably, owing to depolymerisation.

C. H. B.

Titanium. By T. Koenig and O. v. d. Pfordten (*Ber.*, **22**, 2070—2080; compare *Ber.*, **22**, 1485).—The authors tried to prepare titanium sesquioxide by Friedel and Guérin's method (this Journal, 1876, ii, 46), but with negative results.

Titanic acid was heated for two hours with sodium vapour in an atmosphere of pure hydrogen, and the product was washed with alcohol until the washings were free from alkali. A dark-green substance containing 2·58 to 4·93 per cent. of water is obtained; when ignited in the air it lost 2·15 to 5·28 per cent. in weight. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid, yielding a brown solution, which gives the reaction for titanium oxide with thiocyanates (compare v. d. Pfordten, Abstr., 1887, 337). After having been washed with water, it contained as much as 11 per cent. of water.

When the compound $TiCl_3OH$ is heated with sodium vapour under the same conditions and the product washed with water, a black substance containing 10 to 17·1 per cent. of water is obtained; its weight is decreased by 2·49 to 3·18 per cent. on ignition.

In other experiments, the excess of sodium in the crude product was removed by distilling in an atmosphere of hydrogen. The substance obtained in this way increases 1·20 to 3·25 per cent. in weight on ignition, and the ratio of sodium to titanium in the residue is 1 : 1·9. When it is treated with dilute acids, some of the titanium dissolves with a violet coloration, and a black residue remains, the weight of which is increased 2·34 to 3·11 per cent. on ignition. The original substance contains sodium and titanium in the ratio 1 : 3·01 to 1 : 2·85.

These results seem to show that it is probable that the compound formed by the action of sodium on titanic acid has the composition TiO_3Na_3, but it also contains titanium monoxide, and, in addition, unchanged titanic acid.

When titanic iron is heated with sodium under the same conditions, the product, after having been washed with alcohol, is completely soluble in dilute acids, with evolution of hydrogen (= $\frac{1}{2}$ mol. Fe), giving a violet solution in which the ratio of the various constituents is approximately Ti : Fe : Na : O = 1 : 1$\frac{1}{2}$: 1 : 3; the composition of this substance may be expressed by the formula $TiO_3NaFe + \frac{1}{2}Fe$ admixed. It is not acted on by alcohol, but it is decomposed by water, and is then only partially soluble in acids. These results are fresh evidence in favour of the author's view of the constitution of titanic iron.

A number of experiments were made on the reduction of solutions of the trichloride $TiCl_3OH$, titanic acid, and potassium fluotitanate by sodium amalgam in an atmosphere of hydrogen. The subsequent titration of the solutions with potassium permanganate showed that the sesquioxide is formed in every case, and the observation, that solutions of this oxide possess a green or violet colour according to the conditions of their formation, was confirmed. F. S. K.

Fluorine-compounds of Vanadium and its Analogues. By E. PETERSEN (*J. pr. Chem.* [2], **40**, 193—201).—*Vanadyl difluoride*, VOF_2, obtained by dissolving vanadium dioxide in hydrofluoric acid and evaporating, forms blue, microscopic, prismatic crystals (with x mols. H_2O).

Ammonio-vanadyl fluorides. (*a*), $3NH_4F,VOF_2$, is formed by mixing solutions of ammonium fluoride and vanadyl difluoride; it crystallises in blue, microscopic octohedra; it is moderately soluble in water, more sparingly in alcohol; (*b*), $2NH_4F,VOF_2 + H_2O$, obtained when solutions of the calculated quantities of the salt (*a*) and vanadyl difluoride are evaporated together over sulphuric acid, has been already described by Baker (Trans., 1878, 395); and the salt (*c*), $7NH_4F,4VOF_2 + 5H_2O$, crystallises from a solution of equal mols. of ammonium fluoride and the salt (*a*); it is dark-blue, and loses all its water, but no ammonia, at 100°.

When the salt (*a*) is dissolved in strong hydrofluoric acid (35 per cent.), bluish-green microscopic prisms separate: these crumble down to a greenish-grey powder when dry, evolving a smell of hydrogen fluoride. This salt is probably ammonium vanadium tetrafluoride; when dried at 100° it becomes $2NH_4F,VOF_2$.

The author has also obtained, in a similar way, the *potassio-vanadyl fluorides*, $7KF,3VOF_2$ and $2KF,VOF_2$; and the *sodio-vanadyl fluoride*, $8NaF,3VOF_2 + 2H_2O$. A. G. B.

The Basicity of Antimonic Acid. By F. BEILSTEIN and O. v. BLÄSE (*Chem. Centr.*, 1889, 803—806, from *Melanges Phys. Chim. Bull. St. Petersbourg*, **13**, 1—20).—In order to prepare a number of antimonates, the authors employed Dexter's method (*Ann. Phys.*

Chem., **100**, 564) for the preparation of potassium antimonate, which consists in gradually introducing equal parts of dehydrated tartar emetic and potassium nitrate, well mixed together, into a red-hot crucible and gradually adding a half part of potassium hydroxide, after which the mass is kept in a fused state for half an hour, and then extracted with water. From the potassium salt thus obtained, the following salts were prepared by double decomposition. Generally these are sparingly soluble or insoluble in water and uniformly contain water of crystallisation, a part of which is liberated at 100°. The remainder is dissipated by heating strongly, without, however, the salt losing any oxygen. Some of them become incandescent when losing the water of combination, and, after suffering the loss of this water, they become insoluble in menstrua in which they were soluble when freshly prepared.

Lithium antimonate, $LiSbO_3 + 3H_2O$, which is precipitated in the form of hexagonal plates, loses all its combined water by ignition, and retains its white colour. *Mercuric antimonate*, $Hg(SbO_3)_2 + 6H_2O$, is a slowly separating light precipitate, which becomes yellow on decanting and black when heated. *Aluminium antimonate*, $Al(SbO_3)_3 + 15H_2O$, forms shining microscopic crystals after remaining in the solution several days; at 100° it loses 5 mols. H_2O, at 150° $2\frac{1}{2}$ mols. more, and at 200° it retains only 3 mols., whilst it becomes incandescent. *Thallium antimonate*, $TlSbO_3 + 2H_2O$, forms colourless needles, somewhat soluble in water when freshly precipitated, but insoluble when dried; it loses 1 mol. H_2O at 100° and the remainder at 150°, at the same time becoming incandescent. On heating it becomes lemon-yellow, then dark-orange, recovering its colour again when cold. *Lead antimonate.*—That prepared from lead acetate, is a colourless precipitate, having the formula $2Pb(SbO_3)_2,PbO + 11H_2O$, and appears to suffer a partial decomposition with water. From lead nitrate a salt, $Pb(SbO_3)_2 + 6H_2O$, is obtained. *Chromic antimonate*, $Cr(SbO_3)_3 + 14H_2O$, is a bluish, readily-washed precipitate which becomes grey when heated. *Manganese antimonate*, $Mn(SbO_3)_2 + 7H_2O$, is a colourless precipitate, becoming black and incandescent when heated. *Ferrous antimonate* could not be prepared free from the oxide. *Ferric antimonate*, $Fe_2O_3,2Sb_2O_5 + 11H_2O = OH{\cdot}Fe(H_2SbO_4)_2 + 3H_2O$, prepared from iron ammonium alum, is a yellow salt which loses its water of combination at 100°. From ferric chloride, a light yellow salt of the formula $Fe(SbO_3)_3 + 6\frac{1}{2}H_2O$ was obtained. *Cupric antimonate* varies in composition according to the manner of preparation; $3CuO,2Sb_2O_5 + 13H_2O$ is obtained from cupric sulphate, by repeatedly washing the pale-green precipitate, during which process it becomes more and more basic, finally attaining to the above constitution. *Silver antimonate*, $AgSbO_3 + 3H_2O$, is a colourless amorphous precipitate, readily soluble in ammonia when freshly prepared, but almost insoluble after drying; it loses 2 mols. of H_2O at 20°, the remainder only at a high temperature. *Ammonio-silver antimonate*, $AgSbO_3,2NH_3 + 2H_2O$, is prepared by passing dry ammonia over the last named air-dried salt. The authors could not prepare antimonates of the organic radicals.

They conclude that antimonic acid is monobasic, and that the only well known series of antimonates are derived from the monobasic orthoantimonic acid.

Dexter's method is recommended for the preparation of a solution of potassic antimonate to be used as a reagent for sodium.

J. W. L.

Action of Silicon on Gold, Silver, Platinum, and Mercury.

By H. N. WARREN (*Chem. News*, **60**, 5—6).—A brittle and fusible platinum silicide is formed, not only when nascent silicon, but also when graphitoïdal silicon, is heated at a full red heat with platinum, or when a mixture of amorphous silicon and platinum black is heated in a crucible under a layer of potassium silicofluoride; by the latter method a regulus containing 10 per cent. of silicon may be obtained. In a similar manner, gold or silver silicide is formed when gold or silver is heated at a high temperature with a mixture of potassium silico-fluoride and sodium. The gold regulus containing 5 per cent. of silicon is as brittle as antimony. Although neither gold nor silver in a pure state has any great affinity for silicon, yet when they contain a little silicide, they combine with that element readily. Silver with 10 per cent. of silicon has a red tint, and when pulverised is completely decomposed by concentrated hydrochloric acid.

D. A. L.

Platinates of the Alkalies and Alkaline Earths.

By G. ROUSSEAU (*Compt. rend.*, **109**, 144—146).—If barium oxide mixed with an equal quantity of the chloride or bromide is heated for several hours at 1100° in an open platinum crucible, a considerable quantity of crystallised barium platinate is formed. It has the composition $3BaO,PtO_2$, and is more readily obtained in crystals by first producing the amorphous platinate by heating platinic chloride with barium oxide, and then adding a sufficient quantity of barium chloride or bromide and heating at the melting point of copper. The alkalinity of the mixture has great influence on the crystallisation. The crystals are prisms with hexagonal bases, and are insoluble in acetic acid, but dissolve in hydrochloric acid. At an orange-red heat, in presence of barium chloride, the platinate decomposes and metallic platinum separates.

Amorphous sodium platinate formed by the action of platinic chloride on sodium hydroxide does not crystallise even at a temperature sufficient to volatilise the excess of alkali. The crystallised salt can, however, readily be obtained by heating a mixture of equal parts of sodium hydroxide and chloride in a platinum crucible at the melting point of copper for two hours. In order to avoid the destruction of the crucible, it is advisable to add finely-divided platinum to the mixture. If the platinate which forms is continually stirred into the molten mass, it separates in brownish-yellow, microscopic lamellæ, which have a feeble action on polarised light and dissolve readily in hydrochloric acid. If, however, the platinate is allowed to collect in a ring at the surface of the fused mass, it forms much larger reddish-brown, hexagonal lamellæ, which dissolve with difficulty in hydrochloric acid. The composition of the two products is as follows:—

	PtO_2.	Na_2O.	H_2O (by diff.).
(1)	87·02	2·33	10·65
(2)	86·69	5·34	7·97

These platinates become anhydrous at 200—300°, and at a dull-red heat decompose with separation of metallic platinum and sodium hydroxide.

The stability of the platinates is of the same order as that of the manganates and ferrates, and the composition of the latter is almost identical with that of the corresponding platinum compounds.

C. H. B.

Organic Chemistry.

Elimination of Carbonic Anhydride by the aid of Sodium Methoxide. By I. Mai (*Ber.*, **22**, 2133—2136).—The distillation of salts of complex fatty acids with soda-lime with the object of eliminating carbonic anhydride does not in all cases lead to the production of the corresponding hydrocarbon; thus barium palmitate, when heated with soda-lime in a vacuum, yields no appreciable quantity of pentadecane, but forms other decomposition products and in particular ketones. The author finds, however, that if sodium methoxide is substituted for soda-lime and the distillation is performed in a vacuum, carbonic anhydride is readily eliminated from the fatty acid with the production of the hydrocarbon; under these conditions barium myristate, palmitate, and stearate yield tridecane, pentadecane, and heptadecane respectively. The reaction is not confined to the acids of the paraffin series; thus barium benzoate is readily converted into benzene when heated with sodium methoxide, and the decomposition takes place at a lower temperature than with soda-lime. The corresponding unsaturated hydrocarbons can also be obtained from complex unsaturated fatty acids when these are heated with sodium methoxide in a vacuum, and the reaction differs therefore from that which takes place when these acids are heated with caustic soda. Barium erucate under these conditions yields a hydrocarbon, $C_{21}H_{42}$, which boils at 201—202° under a pressure of 11 mm., and has a sp. gr. = 0·8048 at 15°, 0·8015 at 20°, and 0·7981 at 25°, whilst barium elaidate forms a *heptadecylene*, $C_{17}H_{34}$, which boils at 160° under a pressure of 9·5 mm., and has a sp. gr. = 0·8042 at 0°, 0·8006 at 6°, and 0·7977 at 10°.

Bibasic acids can be converted into monobasic acids by the partial action of sodium methoxide; thus barium sebacate and succinate yield nonylic and propionic acids respectively when heated with the methoxide, in molecular proportion, at 300° for 2 to 3 hours.

W. P. W.

Liquefaction of Propylene, Allylene, and Trimethylene. By N. Moltschanoffsky (*J. Russ. Chem. Soc.*, 1889, **21**, 31—32).—For compressing the gases, Cailletet's apparatus was used. The pressures required for liquefaction at the ordinary temperature were :—

Propylene	7–8 atm.
Allylene	3–4 „
Trimethylene	5–6 „

B. B.

Amylene from Tertiary Amyl Iodide. By I. Kondakoff (*J. Russ. Chem. Soc.*, 1889, **21**, 78—79).—As Wagner has shown that two hydrocarbons are formed when the elements of hydrogen iodide are removed from tertiary and secondary alkyl iodides, the author has changed the opinion he formerly held, and now finds that tertiary amyl iodide really yields a mixture of trimethylethylene with asymmetric methylethylethylene.

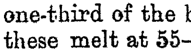
The author treated amylene from the tertiary iodide with chlorine and decomposed the product with a solution of potassium carbonate. On oxidising the alcoholic solution with silver oxide, silver methylethylacetate was obtained, so that the solution must have contained primary angelic alcohol; this could only have been formed from asymmetric methylethylethylene. In this way Wagner's view was fully confirmed. B. B.

Action of Hydrogen Chloride on Dimethylallylene. By I. Kondakoff (*J. Russ. Chem. Soc.*, 1889, **21**, 36—37).—Dimethylallylene, prepared by heating trimethylethylene monobromide (b. p. 114—125°) with caustic potash at 145° was found to boil at 46—48° (and not at 39—40°, as stated by Favorsky, Abstr., 1888, 799). It combines easily at 0° with gaseous hydrogen chloride, forming a chloride, C_5H_9Cl. On treating this with water, an alcohol is obtained which boils at 97—100°, and combines with bromine to form a compound, $C_5H_{10}OBr_2$. On heating dimethylallylene with fuming hydrochloric acid at 80—90°, several compounds (chlorides) were obtained, and these, on treatment with aqueous potash, yielded products from which an alcohol was obtained. This the author proposes to investigate and compare with the derivatives of isoprene obtained from caoutchouc. B. B.

Action of Zinc Ethyl on Primary and Secondary Nitro-compounds. By I. Bevad (*J. Russ. Chem. Soc.*, 1889, **21**, 43—47).—In a former paper (this vol., p. 112), the author showed that the product of the action of zinc ethyl on nitroethane is a compound of the formula $C_6H_{15}NO$; this the author considers to be $Et_3N\colon O$, that is, the isomeride of triethylhydroxylamine, $Et_2N\cdot OEt$, for on treating it with nascent hydrogen (zinc and sulphuric acid) and then with potash, triethylamine was obtained. With zinc ethyl, nitropropane first forms an additive compound of the formula $Et_2PrN(O\cdot ZnEt)_2$, and then a compound having the constitution $Et_2PrN\colon O$. This has a sp. gr. of 0·888 at 0°, and on reduction gives diethylpropylamine. Primary nitropentane, under similar conditions, yields an analogous compound. The products obtained from zinc ethyl and nitroisopropane are first $Et_2PrN(O\cdot Et)_2$ and then $Et_2PrN\colon O$. Aromatic nitro-compounds (being tertiary compounds) behave in quite a different manner, nitrobenzene yielding aniline. B. B.

Preparation of Secondary and Tertiary Nitro-compounds from Halogen-derivatives of Nitromethane and Nitroethane. By I. Bevad (*J. Russ. Chem. Soc.*, 1889, **21**, 47—50).—Monobromonitroethane and zinc ethyl in ethereal solution yield nitroisopropane. Under similar circumstances dibromonitroethane yields nitrobutane, only one bromine-atom being substituted by the ethyl-group, the second by hydrogen. B. B.

Hexabromotetramethylene. By A. Sabanéeff (*J. Russ. Chem. Soc.*, 1889, **21**, 1—7).—In 1882, Reboul observed that when acetylene is passed into bromine, tetrabromacetylene is obtained together with a solid substance of the empirical formula C_2HBr_3. The author has found that the formation of the latter depends on the temperature of the bromine, for, if the bromine is kept well cooled, none of this substance is formed, whereas, if acetylene is passed into boiling bromine, as much as 6 per cent. of the crystalline substance is obtained. A comparison of this substance with ordinary tribromacetylene (b. p. 162—163°) has convinced the author that it is a polymeric modification of it, $(C_2HBr_3)_n$. It is very sparingly soluble in tetrabromacetylene, still less in alcohol, but more soluble in ether, and easily in carbon bisulphide, chloroform, and benzene. When recrystallised from hot benzene, it forms glistening, rhombic scales; it melts at 172—174°, and volatilises at about 250° with decomposition. From vapour-density determinations, it is found that the polymeric tribromacetylene begins to dissociate at 170°, and at 250° values are obtained lying midway between those required by the formulæ $(C_2HBr_3)_2$ and C_2HBr_3. On boiling its solution in benzene with molecular silver, one-third of the bromine is removed and yellow needles are obtained; these melt at 55—56°, and have the formula $(C_2HBr_2)_n$. The molecular formula of the polymeric tribromethylene was determined by Raoult's freezing method in a benzene solution, and found to be $C_4H_2Br_6$. It does not combine with bromine, and must therefore be regarded as a derivative of tetramethylene. The author explains the formation of this compound as follows:—(1) $C_2H_2 + Br_2 = C_2HBr + HBr$; (2) $C_2HBr + C_2HBr = C_4H_2Br_2$; and (3) $C_4H_2Br_2 + 2Br_2 = C_4H_2Br_6$. The hexabromotetramethylene is regarded by the author as a symmetrical compound of the formula



B. B.

Vapour Density of Ethyl Isocyanurate at Different Temperatures. By S. Krapivin and N. Zelinsky (*J. Russ. Chem. Soc.*, 1889, **21**, 66—73).—Troost and Hautefeuille have shown that isocyanuric acid can be converted into isocyanic acid and *vice versâ*, but, as nothing is known as to the conditions under which the conversion of alkyl isocyanurates into isocyanates takes place, the authors have investigated the behaviour of ethyl isocyanurate at high temperatures. The ethyl salt was prepared by the action of dipotassium hydrogen cyanurate on potassium ethyl sulphate and recrystallisation of the product from dilute alcohol. The theoretical vapour-density of the compound $(EtNCO)_3$ is 7·378. The density found by Hoffmann's method was 7·36 at 192°; 7·32 and 7·46 at 210°. Dumas' method gave 7·58 at 305°, and 7·44 at 335°; whilst V. Meyer's method gave 7·49 at 444°. On repeating the experiment, decomposition, consisting in a depolymerisation, was found to take place after the first normal evolution of displaced gas, as shown by the numbers obtained, namely, 5·72 and 5·15 at 444°. On cooling, however, the substance was found in its original state. This result was confirmed by many other experiments at the same temperature. In the vapour of phosphorus pentasulphide, numbers varying from 1·87—7·62 were obtained, according as to whether the displaced gas measured was collected during the first normal evolution of gas, or for some time afterwards when decomposition had taken place. The substance which remained on cooling was always found to have a strong smell of the cyanate, EtNCO. On using the method of displacement of Wood's alloy at 518°, results approaching the number 2·46, that is, the theoretical vapour-density of EtNCO, were obtained. The authors conclude that ethyl isocyanurate is capable of bearing high temperatures for a short time without change, its vapour being stable for a few moments even at 518°; on continued heating, however, at this high temperature it is dissociated into the isocyanate, the quantity of the latter increasing with the duration of heating. B. B.

Double Thiocyanates of Iron and Potassium. By G. Krüss and H. Moraht (*Ber.*, **22**, 2061—2065; compare p. 1247).—Various double thiocyanates of iron and potassium can be prepared by dissolving freshly-precipitated and well-washed ferric hydrate in a quantity of hydrogen thiocyanate exactly sufficient for complete solution, adding the calculated quantity of potassium thiocyanate, and evaporating the solution under reduced pressure over sulphuric acid. The compounds described below were obtained in this way.

The *salt* $Fe(CNS)_3,9KCNS + 4H_2O$ crystallises from cold water in long, dark-red, rhombic prisms with a greenish reflex, and is moderately stable, although it slowly deliquesces on exposure to moist air. The solution in pure water is stable, but in presence of traces of sodium chloride, ammonium chloride, and other salts, and also of free hydrochloric acid, the double salt is partially decomposed. It is insoluble in anhydrous ether, but in presence of a very small quantity of water it first dissolves and is then rapidly decomposed into its constituents, the potassium thiocyanate separating in colourless crystals, whilst the ferric thiocyanate remains dissolved in the ether.

The *salt*, $Fe(CNS)_3,3KCNS$, crystallises in small, hexagonal crystals, and is much lighter in colour than the preceding compound. It is exceedingly hygroscopic, and only the ratio of iron to potassium could be determined. The aqueous solution has an intense red colour, and gives the same reactions as a solution of the preceding compound.

When a solution of 1 mol. of ferric thiocyanate and more than 9 mols. of potassium thiocyanate is evaporated over sulphuric acid, the salt $Fe(CNS)_3,9KCNS + 4H_2O$ separates from the solution at first, and eventually crystals of potassium thiocyanate are obtained.

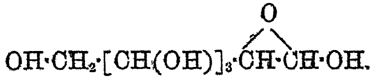
Ferric thiocyanate cannot exist in the free state in solutions containing potassium thiocyanate; when a solution of ferric thiocyanate is diluted with distilled water, until only a slight yellow coloration is perceptible, and then treated with a concentrated solution of potassium thiocyanate, the dark, cherry-red coloration due to the formation of the double salt is immediately produced. F. S. K.

Stability of Fatty Glycerides. By T. T. P. B. Warren (*Chem. News*, **60**, 42).—It is known that the drying or clogging properties of oils are due to their becoming oxidised. Poppy-seed and walnut oils thicken readily on exposure to warm air; cotton and rape-seed oils suffer a similar change when heated air or oxygen is passed through them; olive oil, however, does not thicken under the same circumstances, and is, in fact, more stable than sesame oil.

When these oils oxidise, their iodine absorption diminishes, their electrical resistance increases, and their behaviour with sulphur chloride changes. A clogging oil is, of course, unsuitable for lubricating; it is therefore convenient to be able to decide as to the suitability of an oil for this purpose by simply noting its iodine absorption before and after submitting it to the action of oxygen.

D. A. L.

Constitution of Dextrose. By Z. H. Skraup (*Monatsh.*, **10**, 401—410).—Dextrose is commonly regarded as being a pentahydric alcohol aldehyde, but Fittig, and, more recently, Tollens, have called attention to the fact that it may also be considered as an ether derived from a heptahydric alcohol, and as having the formula



$$\mathrm{OH{\cdot}CH_2{\cdot}[CH(OH)]_3{\cdot}}\overbrace{\mathrm{CH{\cdot}CH}}^{\mathrm{O}}\mathrm{{\cdot}OH}.$$

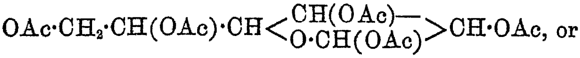
The author has made a series of experiments with the pentabenzoylderivative, described by him (p. 1152), and with the sugar itself, which lead to the conclusion that Fittig's view is probably the correct one.

Phenylhydrazine at ordinary temperatures is without action on pentabenzoyldextrose dissolved in alcohol or suspended in ether, but in a solution of benzene the two react giving rise to the production of E. Fischer's benzoylphenylhydrazine (*Annalen*, **190**, 126), melting at 169°, and a resinous product. On treatment with a 5 per cent. solution of permanganate in acetic acid, pentabenzoyldextrose is not oxidised to pentabenzoylgluconic acid; hence it must be concluded that pentabenzoyldextrose is not an aldehydic compound. This view is confirmed by the fact that dextrose on treatment with phenylhydrazine furnishes two dextrosephenylhydrazines, melting at 144—146° and 115—116° respectively, one of which is probably derived from the compound $C_6H_{12}O_8$, the other from the compound $C_6H_{12}O_6,H_2O$. The former derivative is sparingly soluble in alcohol and crystallises in minute microscopic plates, the latter dissolves readily in water and hot alcohol, but is insoluble in ether, and when pure is unchanged by exposure to air and light. When warmed with phenylhydrazine acetate in aqueous solution, characteristic needles of phenylglucosazone, melting at 206°, are formed.

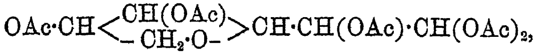
The author suggests that the so-called water of crystallisation in sugars, like milk sugar and maltose, may probably bear the same relation to the molecule as in the case of dextrose. G. T. M.

Pentacetylgalactose and Pentacetyldextrose. By E. ERWIG and W. KOENIGS (*Ber.*, **22**, 2207—2213; compare this vol., p. 952).—*Pentacetylgalactose*, $C_6H_7O(OAc)_5$, is formed when galactose (20 grams) is carefully heated with fused sodium acetate (10 grams) and acetic anhydride (100 c.c.) until the somewhat vigorous reaction ensues, and the mixture is then boiled for about 10 minutes in a reflux apparatus. The solution is concentrated on a water-bath, the residue evaporated twice with alcohol to free it from acetic acid and acetic anhydride, then extracted with water to remove sodium acetate, purified by boiling in alcoholic solution with animal charcoal, and finally crystallised from alcohol. The yield amounts to 60 per cent. of the galactose employed. The presence of sodium acetate is necessary to secure a good yield, since in its absence the amount of the pentacetyl-derivative obtained is very small. Acetylation in the presence of zinc chloride in small quantity results in the formation of a non-crystallisable compound, which is also formed when pentacetylgalactose is boiled with zinc chloride and acetic acid. Pentacetylgalactose crystallises in colourless, compact, lustrous, rhombic prisms. $a : b : c = 0{\cdot}92764 : 1 : 1{\cdot}3951$, observed faces OP (predominating), ∞P, $\breve{P}\infty$, and $\bar{P}\infty$, melts at 142° and is readily soluble in benzene, chloroform, acetic acid, and ethyl acetate, moderately soluble in ether, hot alcohol, and hot water, and sparingly soluble in carbon bisulphide and light petroleum. It reduces Fehling's solution rapidly on warming, is dextro-rotatory in chloroform solution, and differs in all its properties from Fudakowsky's pentacetylgalactose (Abstr., 1878, 777).

Pentacetylgalactose and pentacetyldextrose closely resemble one another in their behaviour with various reagents. When boiled with decinormal sulphuric acid, they undergo hydrolysis with the regeneration of the carbohydrates from which they are prepared, but they are not changed by prolonged boiling with water. They do not give the aldehyde reaction with a solution of magenta decolorised with sulphurous acid, do not form hydrazones with phenylhydrazine or oximes with hydroxylamine under very varied conditions, and are not acted on by phosphorus pentachloride in boiling chloroform solution. They are not oxidised on treatment with bromine in dilute acetic acid solution under the conditions employed by Kiliani in the preparation of galactonic and gluconic acids (Abstr., 1884, 993; 1885, 967), but on treatment with potassium dichromate and acetic acid on a water-bath, or with potassium permanganate, they are slowly and completely oxidised, the pentacetylgalactose more rapidly than the pentacetyldextrose, with the evolution of carbonic anhydride, no other acids than acetic acid being apparently formed. These results, in the authors' opinion, indicate that these pentacetyl-derivatives do not contain the aldehyde-radicle, and afford a further argument in favour of the lactonic constitution of galactose and dextrose advocated by Tollens (*Ber.*, **16**, 921) and Sorokin (*J. pr. Chem.*, [2], **37**, 312). Which of the two formulæ



$$OAc\cdot CH_2\cdot CH(OAc)\cdot CH{<}\begin{matrix}CH(OAc)-\\O\cdot CH(OAc)\end{matrix}{>}CH\cdot OAc, \text{ or}$$



$$OAc\cdot CH{<}\begin{matrix}CH(OAc)\\-CH_2\cdot O-\end{matrix}{>}CH\cdot CH(OAc)\cdot CH(OAc)_2,$$

should be adopted for the pentacetyl-derivatives cannot yet be decided, but in favour of the former it is noted that the production of hexacetylmannitol by acetylation under conditions similar to those employed in the preparation of these pentacetyl-derivatives (Franchimont, Abstr., 1880, 104) takes place without the formation of an "inner anhydride," which must occur if pentacetyldextrose is represented by the latter formula.

Pentacetyldextrose is not obtained by boiling Herzfeld's octacetylmaltose (Abstr., 1884, 171) with acetic anhydride and a small quantity of zinc chloride. The conversion of octacetyldiglycose into pentacetyldextrose under these conditions is accompanied by inversion, and the authors find that inversion takes place when cane sugar and inulin are acetylated in like manner, and that the inversion of both is rapidly effected by treatment with a half or 1 per cent. aqueous solution of zinc chloride on a water-bath. W. P. W.

Formation of Cane Sugar from Starch. By F. SELIVANOFF (*J. Russ. Chem. Soc.*, 1889, **21**, 27—31).—In this purely theoretical paper the author tries to prove that, in plants, starch may be converted into cane sugar and *vice versâ*. B. B.

Oxidation of Maltose. By E. FISCHER and J. MEYER (*Ber.*, **22**, 1941—1943; compare this vol., p. 485).—*Maltobionic acid*, $C_{12}H_{22}O_{12}$, is formed when maltose (1 part) is treated with bromine (1 part) in aqueous solution at the ordinary temperature. It is an almost colourless, strongly acid syrup, very readily soluble in water, but only moderately so in alcohol and insoluble in ether. It does not reduce Fehling's solution and it is very similar to lactobionic acid in its properties. The salts, prepared by neutralising the acid with metallic carbonates, are all readily soluble in water and do not crystallise readily. The *calcium* salt, $(C_{12}H_{21}O_{12})_2Ca$, is a colourless, semi-crystalline compound.

When maltobionic acid is heated at 100° for an hour with 5 per cent. sulphuric acid (5 parts), it is completely decomposed into dextrose and gluconic acid.

These experiments show that maltose, like lactose, contains an aldehyde group, and this fact lends support to the view previously expressed (Abstr., 1888, 1267) that lactose and maltose have the same constitution. F. S. K.

The Birotation of Arabinose and its Reducing Value with Fehling's and Sachsse's Solutions. By R. W. BAUER (*Landw. Versuchs-Stat.*, **36**, 304).—The rotatory power of arabinose was found to be $[\alpha]D = 116{\cdot}75$ in a freshly prepared solution, 108·75 after the lapse of 5 hours, and 104·4 after 36 hours. 100 c.c. of Fehling's solution is reduced by 0·4303 gram of arabinose; the amount of dextrose required is 0·4753 gram, 100 c.c. of Sachsse's solution is reduced by 0·4375 gram of arabinose, which is nearly the same as the amount of galactose (0·4420 gram) required.

A 0·5 per cent. solution of arabinose has a distinctly sweet taste.

N. H. M.

Combination of Cupric Oxide with Starches, Sugars, and Mannitols. By C. E. GUIGNET (*Compt. rend.*, **109**, 528—530).—A solution of cellulose in ammonio-cupric oxide is precipitated by a large quantity of water and yields a somewhat well-defined compound of cellulose and cupric oxide, from which ammonia can be completely removed by washing.

Dry starch or flour readily absorbs cupric oxide from ammonio-cupric oxide solution, and decolorises the liquid, the action being more rapid if the starch has previously been slightly moistened. Starch paste acts in the same way, although less rapidly. A deep-blue compound is formed, from which water and even dilute ammonia remove only traces of copper. It retains ammonia, which it loses if heated with water at 40°, becoming pale blue. At 80°, starch paste is formed and retains anhydrous cupric oxide so intimately mixed with it that under the microscope each starch granule is seen to be covered with a dark grey pellicle. After prolonged digestion with strong ammonia, the compound of cupric oxide and starch dissolves and the liquid contains cupric oxide and soluble starch.

Inulin behaves in a similar manner.

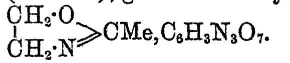
Ammonio-cupric oxide gives no precipitate with sugars, but a solution of cuprammonium sulphate, free from excess of ammonia, gives, with glucose, galactose, &c., an almost immediate precipitate soluble in excess of the reagent. Saccharose, lactose (and probably their isomerides), invert saccharose, and pure levulose from inulin, give no precipitate. If, however, glucose is added to invert sugar or to levulose the glucose compound is precipitated after some hours, a result which seems to indicate that invert sugar is a compound and not a mere mixture of levulose and glucose. After prolonged washing with water, the glucose compound contains no ammonia; it is very slightly soluble in water but dissolves readily in ammonia, and after some days at the ordinary temperature, or almost immediately if heated, the solution becomes colourless, without precipitation of cuprous oxide; the liquid then contains a salt which is very soluble in water and somewhat soluble in alcohol, and which has the properties of ammonium gluconate. It follows that if ammonium chloride is added to Fehling's solution in the titration of glucose, the free ammonia which is liberated may prevent the reduction of a small quantity of the glucose.

Mannitol, dulcitol, and probably their isomerides produce immediate blue precipitates with cuprammonium sulphate; these dissolve in ammonia with formation of blue solutions which are not affected by ebullition under ordinary pressure.

Cuprammonium sulphate gives no precipitate with vegetable acids, gums, pectic substances, and most other compounds found in vegetable extracts. It may, therefore, be employed with advantage in many cases in place of normal or basic lead acetate. In the case of alcoholic solutions, cuprammonium acetate must be used.

Cuprammonium sulphate is gradually precipitated by large quantities of water. Cuprammonium oxide should be made according to Peligot's directions, by the action of ammonia on cupric hydroxide.

C. H. B.

Bromethylamine. By S. Gabriel (*Ber.*, **22**, 2220—2223).—When a mixture of bromethylamine hydrobromide (5 grams) and dry sodium acetate (1 gram) is boiled for five minutes with acetic anhydride (15 c.c.), and the product, after filtration from the separated sodium bromide, is concentrated on a water-bath, a syrup is obtained which, on treatment with a decinormal solution of sodium picrate (100 c.c.), gives a small yield (0·25 gram) of *methyloxazoline picrate*,  $\begin{matrix}CH_2\cdot O\\ | \\ CH_2\cdot N\end{matrix}\!>\!CMe,C_6H_3N_3O_7$. This crystallises in yellow scales, begins to sinter at 145°, melts at 147—149°, and on treatment with aqueous potash yields the base, which has a peculiar, sweet odour somewhat recalling that of quinoline. When boiled with water, the picrate is converted into *hydroxyethylacetamide picrate*,

$$OH\cdot CH_2\cdot CH_2\cdot NHAc,C_6H_3N_3O_7,$$

crystallising in long, compact needles melting at 167—169°. Both picrates can be obtained by treating a benzene solution of bromethylamine with acetic anhydride, evaporating the solution to a syrup on the water-bath, and adding a solution of sodium picrate; the methyloxazoline picrate crystallises out within a short time, and the mother-liquor, after filtration, slowly deposits the hydroxyethylacetamide picrate in compact prisms during the following 12 hours.

β-Bromethylbenzamide, $CH_2Br\cdot CH_2\cdot NHBz$, is formed by shaking benzoic chloride (6 grams) with a mixture of bromethylamine hydrobromide (6 grams) and $\frac{1}{5}$-normal aqueous soda (150 c.c.) in the cold, and subsequently adding a like quantity of the aqueous soda; a white, crystalline powder (4·5 grams) separates, which, on crystallisation from benzene or ethyl acetate, melts at 105—106°. When boiled with water, it at first melts and afterwards dissolves with the formation of *hydroxyethylbenzamide hydrobromide*, $OH\cdot CH_2\cdot CH_2\cdot NHBz,HBr$, which crystallises from alcohol in lustrous tables melting at 142—143°. The *base* is an oil soluble in chloroform; the *platinochloride*,

$$(C_9H_{11}NO_2)_2,H_2PtCl_6,$$

crystallises in sparingly soluble, flat, yellow needles; the *picrate* is crystalline, begins to sinter at 180°, and melts at 195°. W. P. W.

Dihydroxyphosphinic Acids. By J. Ville (*Compt. rend.*, **109**, 71—74).—The author has previously shown (this vol., p. 141) that when benzaldehyde is heated with hypophosphorous acid it yields dihydroxybenzylenephosphinic acid. Many other aldehydes behave in the same way, and when heated with hypophosphorous acid at 100° for several hours in an atmosphere of hydrogen, they yield acids of the general formula $PO(CHR\cdot OH)_2\cdot OH$. These compounds have no reducing action on ammoniacal silver nitrate or copper sulphate, and when heated somewhat above their melting points they split up into the corresponding aldehyde, hydrogen phosphide, and a bulky residue of carbon. They are monobasic acids with a double alcoholic function.

Dihydroxyœnanthylphosphinic acid, $PO[CH(C_6H_{13})\cdot OH]_2\cdot OH$, forms white, transparent lamellæ, which melt at 160°, and are only slightly soluble in water, but dissolve readily in strong alcohol. It is a strong acid, and yields well defined salts. When distilled with water and manganese dioxide, it yields œnanthol, and when heated in sealed tubes at 135° with dilute sulphuric acid it yields œnanthaldehyde, phosphorous acid, and a small quantity of phosphoric acid. The *barium salt* (3 mols. H_2O) forms slender, microscopic needles, which become anhydrous at 100—105°; they dissolve readily in water, but are only slightly soluble in alcohol. The *potassium salt* crystallises in thin, transparent plates, and the *lead salt* is granulo-crystalline. The *diacetyl-derivative*, $PO[CH(C_6H_{13})OAc]_2\cdot OH$, forms yellowish-white crystals, melts at 94°, and is insoluble in water, but dissolves in alcohol and in ether, from which it crystallises in slender, microscopic needles.

Dihydroxyisoamylphosphinic acid, $PO[CH(C_4H_9)\cdot OH]_2\cdot OH$, forms white needles, which melt at 160°, and are only slightly soluble in water, but dissolve readily in alcohol, from which the acid crystallises in microscopic hexagonal lamellæ. When heated in sealed tubes at 135° with dilute sulphuric acid, and when distilled with water and manganese dioxide, it behaves in the same way as the œnanthyl-derivative. The *barium salt* forms crystalline crusts or slender needles containing 1 mol. H_2O, which is given off at 105°; it is very soluble in water, but only slightly soluble in alcohol. The *potassium salt* crystallises in aggregations of lamellæ, and the *lead salt* is granulo-crystalline. The *diacetyl-derivative* is a thick, syrupy liquid, insoluble in water, but very soluble in alcohol; it is slowly saponified by water, and rapidly by aqueous potash.

Cumaldehyde and salicaldehyde yield analogous compounds.

C. H. B.

Sulphines and the Valency of Sulphur. Part II. By H. Klinger and A. Maassen (*Annalen*, **252**, 241—266); see Abstr., 1888, 357).—Triethylsulphine iodide is converted into trimethylsulphine iodide by the action of methyl alcohol at 130°. The reaction which takes place does not consist in a simple displacement of ethyl by methyl; on the contrary, it appears probable that the triethylsulphine iodide dissociates into ethyl iodide and ethyl sulphide, and these compounds react on the methyl alcohol, forming methyl ethyl ether and methyl iodide. Other intermediate products are also formed. Ethyl alcohol at 140° slowly converts trimethylsulphine iodide into the triethyl-derivative. At 100°, ethyl iodide (1 mol.) and methyl alcohol (2 mols.) yield hydrogen iodide, methyl ethyl ether, and methyl iodide.

Trimethylsulphine iodide is conveniently prepared by the action of powdered sodium sulphide (10 grams) on methyl iodide (15 c.c.) at 100°. The operation can also be carried on in an alcoholic solution.

Methyl iodide acts on cadmium sulphide, yielding the double salt, CdI_2,SMe_3I, crystallising in white needles, and melting at 167—168°. It is easily decomposed by alcohol, ether, or water, forming $CdI_2,2SMe_3I$; this compound melts at 185°, or when rapidly heated at 195°; it also melts in hot water. Ethyl iodide forms a similar compound, melting at 145°. With stannous sulphide, methyl iodide forms the somewhat unstable compound SnI_2,SMe_3I. Methyl iodide acts on arsenious sulphide, forming a mixture of methylarsen tetriodide $AsMeI_4$, and the compound $As_2I_6,3SMeI$. The latter compound forms dark blue crystals. W. C. W.

Disulphones. By E. BAUMANN and A. KAST (*Zeit. physiol. Chem.*, **14**, 52—74).—See p. 1232.

Action of Ethyl Iodide and Zinc on Paraldehyde. By V. WEDENSKY (*J. Russ. Chem. Soc.*, 1889, **21**, 9—13).—Paraldehyde (100 grams) was mixed with ethyl iodide (400 grams) and granulated zinc, and after standing for three months at the ordinary temperature the product was decomposed with water and distilled. A mixture of ethyl and butyl alcohols (probably secondary) was obtained, due probably to the formation of aldehyde. B. B.

Symmetrical Tetrachloracetone. By S. LEVY and A. CURCHOD (*Annalen*, **252**, 330—343).—A convenient method for the preparation of symmetrical tetrachloracetone consists in adding potassium chlorate (16 grams) in small quantities at a time to triamidophenol hydrochloride (20 grams), dissolved in water (30 grams) and hydrochloric acid (86 grams). The tetrachloracetone is extracted from the mixture by ether. The hydrate crystallises in triclinic prisms or plates, $a : b : c = 0{\cdot}93984 : 1 : 1{\cdot}6824$, $\alpha = 100° 2'$; $\beta = 95° 42'$; $\gamma = 122° 28'$. The properties of this compound have been previously described (Abstr., 1888, 444).

Phosphorus pentachloride acts on tetrachloracetone at 100°, yielding symmetrical hexachloropropane and pentachloropropylene. The *hexachloropropane* boils between 184° and 188°, and the *pentachloropropylene* boils about 200°.

Tetrachloracetone ammonia, $OH{\cdot}C(CHCl_2)_2{\cdot}NH_2$, is prepared by passing dry ammonia into an ethereal solution of tetrachloracetone; the ether is removed by evaporation, and the residue purified by recrystallisation from hot benzene. Hydrocyanic acid readily unites with tetrachloracetone to yield the cyanhydrin, the nitril of tetrachlorhydroxyisobutyric acid. The cyanhydrin crystallises in transparent, monoclinic prisms, $a : b : c = 0{\cdot}83004 : 1 : 0{\cdot}68929$, $\beta = 105° 32'$. It is soluble in ether and in warm benzene, chloroform, alcohol, and carbon bisulphide, melts at 112—114°, and begins to decompose about 140°. It is decomposed by water at 100°, and by alkalis at the ordinary temperature, yielding tetrachloracetone and hydrocyanic acid.

The cyanhydrin is converted into the amide of tetrachlorhydroxyisobutyric acid by prolonged boiling with hydrochloric acid. The *amide*, $OH{\cdot}C(CHCl_2)_2{\cdot}CONH_2$, forms colourless prisms, and melts at 156°. W. C. W.

Reduction of Diacetyl. By H. v. PECHMANN (*Ber.*, **22**, 2214).—When reduced with zinc dust and acetic acid in the cold, diacetyl yields the corresponding pinacone as sole product (Abstr., 1888, 812), but if it is boiled with zinc and sulphuric acid, a liquid reduction product is alone formed, which proves on examination to be a ketone-alcohol. *Dimethylketol* (ketone-alcohol), COMe·CHMe·OH, is a colourless liquid, boils at 141—142°, distils without decomposition, reduces Fehling's solution at the ordinary temperature, and is miscible with water. When heated with excess of phenylhydrazine, it yields the osazone of diacetyl.

The term ketol has been adopted by the author as a generic name for those compounds which are simultaneously ketones and alcohols, and its use need not lead to the confusion of ketone-alcohols with Baeyer's methylketole, inasmuch as the latter is now known to be 2′-methylindole, and should be designated as such. W. P. W.

Homologues of Diacetyl. By R. OTTE and H. v. PECHMANN (*Ber.*, **22**, 2115—2126).—The homologues of diacetyl, whose preparation has already been announced (Abstr., 1888, 1052), are most readily obtained from the oximes of the corresponding substituted ethyl acetoacetates by the method adopted in the case of diacetyl (v. Pechmann, Abstr., 1888, 811). In certain cases, when dealing with the higher members, it is necessary to purify the diketones by converting them into the compounds with sodium hydrogen sulphite, which are subsequently distilled with sulphuric acid, and the distillates rectified over potassium carbonate. The average yield of diketone amounts to 30—40 per cent. of the substituted ethyl acetoacetate employed.

The non-aromatic α-diketones, like diacetyl, are yellow oils, which boil without decomposition, do not solidify, and have a quinone-like, and in most cases a somewhat sweet, odour. The solubility in water decreases with the increase in molecular weight. They are characterised by yielding with dilute alkalis colourless solutions, which when warmed become brown with the simultaneous conversion of the diketone into quinone (compare Abstr., 1888, 813). When treated with alcoholic alkalis or potassium cyanide, they decompose with the formation of an acid and an aldehyde, thus resembling benzil under like conditions (Jourdan, Abstr., 1883, 805; Michael and Palmer, Abstr., 1886, 155). Ammonia converts them into substituted glyoxalines; with diazobenzenesulphonic acid, and with a solution of magenta decolorised by sulphurous anhydride they react like aldehydes and ketones; and when shaken with concentrated sulphuric acid and benzene containing thiophen they give rise to a brownish coloration, except in the case of diacetyl, which gives a pure blue.

Acetylpropionyl yields a hydrazone, to which the formula

$$COEt·CMe:N_2HPh$$

has been given, on the ground that it differs from the acetylpropionylhydrazone obtained by Japp and Klingemann by the action of diazobenzene chloride on ethyl ethacetoacetate (Trans., 1888, 540). In view of the fact that V. Meyer has shown that two isomeric benziloximes exist, this negative proof of the constitution of the authors' hydrazone is not entirely satisfactory; the hydrazones could not, however, be converted into one another, and differ, therefore, in their isomerism from the benziloximes. Evidence confirmatory of the formula assigned to the authors' hydrazone, which melts at 102—103°, and not at 96—98°, as previously stated, has been obtained by a study of the acetylpropionylhydrazoximes. When nitrosoethylacetone,

$$COMe\cdot CEt{:}N\cdot OH,$$

is treated with phenylhydrazine, it forms *acetylpropionyl-α-β-hydrazoxime*, $NHPh\cdot N{:}CMe\cdot CEt{:}N\cdot OH$, which is crystalline, melts at 131·5°, and on hydrolysis in alcoholic solution with hydrochloric acid, yields the acetylpropionylhydrazone, melting at 102—103°. The isomeric *acetylpropionyl-β-α-hydrazoxime*, $OH\cdot N{:}CMe\cdot CEt{:}N\cdot NHPh$, prepared from Claisen and Manasse's nitrosodiethyl ketone (this vol., p. 585) by the action of phenylhydrazine, melts at 128°.

Acetylbutyryl (α-β-diketohexane), $COMe\cdot COPr$, obtained from ethyl propacetoacetate by conversion into nitrosopropylacetone and subsequent hydrolysis of the latter, is a yellow oil, which boils at 128°, has a sp. gr. = 0·9343 at 19° (compared with water at 4°), and is less soluble in water than its lower homologues. The *α-hydrazone*, $NHPh\cdot N{:}CMe\cdot COPr$, prepared either by the action of phenylhydrazine on the diketone, or by the hydrolysis of the α-β-hydrazoxime (see further), melts at 113—114°, and is readily soluble in the ordinary solvents, but insoluble in water and light petroleum; the *β-hydrazone*, $COMe\cdot CPr{:}N\cdot NHPh$, formed by the action of diazobenzene chloride on ethyl propacetoacetate, crystallises in colourless needles, and melts at 108—109°; the *αβ-hydrazoxime*, $NHPh\cdot N{:}CMe\cdot CPr{:}N\cdot OH$, obtained by treating nitrosomethyl propyl ketone with phenylhydrazine, crystallises in almost colourless needles, melts at 130·5°, and is soluble in most solvents; the *osazone*, $C_{18}H_{22}N_4$, crystallises from benzene in lustrous yellow needles, and melts at 136·5°; the *dioxime*, $C_6H_{12}N_2O_2$, crystallises in lustrous, white needles, melts at 168°, and is identical with Schramm's methylpropylglyoxime (Abstr., 1884, 52).

Acetylisobutyryl (secondary αβ-diketohexane), $COMe\cdot CO\cdot CHMe_2$, prepared from Westenberger's nitrosomethylisopropyl ketone (Abstr., 1884, 581) is a pungent, yellow oil, which boils at 115—116°, and is sparingly soluble in water.

Acetylisovaleryl (secondary αβ-diketoheptane),

$$COMe\cdot CO\cdot CH_2\cdot CHMe_2,$$

obtained from nitrosoisobutylacetone (Abstr., 1883, 572), is a pungent, yellow oil, which boils at 138°, has a sp. gr. = 0·9082 at 22° (compared with water at 4°), and is sparingly soluble in water. The *hydrazone*, $C_{13}H_{18}N_2O$, crystallises in colourless needles, and melts at 98°; the *αβ-hydrazoxime*, $C_{13}H_{19}N_3O$, crystallises in colourless needles, and melts at 150—151°; the *osazone*, $C_{19}H_{24}N_4$, forms white needles, and melts at 116·5°; the *dioxime*, $C_7H_{14}N_2O_2$, crystallises in lustrous, white scales, and melts at 170—172°.

Acetylcapronyl (secondary αβ-diketo-octane),

$$COMe\cdot CO\cdot CH_2\cdot CH_2\cdot CHMe_2,$$

prepared from nitrosoamylacetone (*ibid.*), boils at 163°, and has a sp. gr. = 0·8814 at 19° (compared with water at 4°). The *hydrazone*, $C_{14}H_{20}N_2O$, crystallises in white needles, melts at 99—100°, and is readily soluble in the usual solvents; the *αβ-hydrazoxime*, $C_{14}H_{21}N_3O$, forms white needles, and melts at 131·5°; the *osazone*, $C_{20}H_{26}N_4$, crystallises in white needles, and melts at 114°; the *dioxime*, $C_8H_{16}N_2O_2$, crystallises in lustrous, white needles, and melts at 172—173°.

Acetylcrotonyl (*αβ*-diketohexylene), $COMe{\cdot}CO{\cdot}C_3H_5$, obtained from ethyl allylacetoacetate by conversion into nitrosoallylacetone and subsequent hydrolysis of the latter, boils at about 130°, but could not be obtained pure, since it cannot be distilled even in a vacuum without partial decomposition. *Nitrosoallylacetone*, $COMe{\cdot}C(N{\cdot}OH){\cdot}C_3H_5$, crystallises in white scales, melts at 46°, is readily soluble in all solvents, and dissolves in aqueous soda with a yellow colour; the *αβ-hydrazoxime* melts at 137°; the *dioxime*, $C_6H_{10}N_2O_2$, forms lustrous scales, and melts at 153°. W. P. W.

Preparation of Acetonylacetone from Ethyl Diacetosuccinate. By L. KNORR (*Ber.*, **22**, 2100—2101; compare this vol., p. 385).—The best yield of acetonylacetone (90 per cent. of that theoretically possible) is obtained by dissolving ethyl diacetosuccinate in 3 per cent. aqueous soda in such proportions that 10 parts of the succinate are present with every 3·1 parts of sodium hydroxide. The reaction is complete at the end of four to six days at the ordinary temperature, but two to three hours only are required for its completion if the solution is heated on a water-bath. The yield is dependent on the amount of alkali present, an excess of which must be avoided. Acetonylacetone can also be readily prepared by heating ethyl diacetosuccinate with 10—20 times its weight of water for about 12 hours at 150—170°; the yield, however, is somewhat less than when alkali is employed, and a small quantity of ethyl pyrotritartrate is also formed during the hydrolysis. W. P. W.

Diethamido-α-propionic Acid. By E. DUVILLIER (*Compt. rend.*, **109**, 149—151).—Diethamido-α-propionic acid,

$$NEt_2{\cdot}CHMe{\cdot}COOH,$$

is obtained by heating α-monobrompropionic acid in sealed tubes at 100° with excess of aqueous diethylamine. It forms bulky, acicular crystals which are as hygroscopic as calcium chloride, and dissolve readily in water and in alcohol; from the latter it is precipitated as a heavy oil on the addition of ether. If the aqueous solution is concentrated, the acid gradually volatilises, and condenses in a snow-like mass on the upper part of the vessel.

The cupric salt crystallises with 1 mol. H_2O in aggregations of brilliant lamellæ of a purple-red colour. They become anhydrous at 110°, and dissolve readily in water and in alcohol. At 100°, the aqueous solution decomposes with separation of reduced copper.

Diethamido-α-propionic acid is the chief product of the action of ethyl iodide on α-amidopropionic acid in presence of alcoholic potash. No ethylpropionic-betaine is formed. C. H. B.

Nitro-compounds of the Fatty Series. By C. C. KOLOTOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 535—536).—In order to study the mechanism of Kolbe's reaction, the author has prepared *ethyl α-nitroisobutyrate*, $NO_2{\cdot}CMe_2{\cdot}COOEt$, by the action of silver nitrite on ethyl α-bromisobutyrate. The nitro-compound, on reduction with tin and hydrochloric acid, yields α-amidoisobutyric acid, $NH_2{\cdot}CMe_2{\cdot}COOH$, and ammonia, the last being probably due to the presence of the metameric nitroso-compound, $NO{\cdot}CMe_2{\cdot}COOEt$, in the crude product. The amido-acid is identical with that described by Urech (*Annalen*, **164**, 255) and by Heintz (*ibid.*, **192**, 352, and **198**, 42). B. B.

Conversion of Oleic Acid into Stearic Acid. By P. DE WILDE and A. REYCHLER (*Bull. Soc. Chim.* [3], **1**, 295—296).—When oleic acid is heated with iodine (1 per cent.) in sealed tubes at 270—280° for several hours, a mixture of crystalline fatty acids is obtained which when distilled in a current of superheated steam yields about 70 per cent. of stearic acid and a liquid fatty acid unalterable by further treatment with iodine.

The iodine probably forms combinations with unsaturated acids which then decompose with liberation of hydrogen iodide; this latter hydrogenises the oleic acid to stearic acid, while iodine is set free.

Bromine (1 per cent.) and chlorine (1·3 per cent.) determine the conversion under like conditions, and this is favoured by the addition of colophony (5 per cent.). T. G. N.

Conversion of Erucic Acid into Behenic Acid. By A. REYCHLER (*Bull. Soc. Chim.* [3], **1**, 296—298).—Pure erucic acid (m. p. 34°) is heated with iodine (1 per cent.) at 270° for four hours; the pale-coloured mass obtained is treated with alcoholic potash, and the soap produced is decomposed by acid: the fatty acids obtained on recrystallisation from alcohol and from ether yield pure behenic acid melting at 77°. T. G. N.

Molecular Weights of the Acids of the Oleic Acid Series. By O. SCHULZ (*Chem. Centr.*, 1889, 781, from *Listy. Chem.*, **13**, 201—203).—The author has determined the molecular weights of crotonic, chlorocrotonic, and chlorisocrotonic acids by means of Raoult's method, and finds that whilst crotonic acid, when determined in aqueous or acetic acid solution, has the formula $C_4H_6O_2$, in benzene solution it exhibits double that molecule. J. W. L.

Regularities in the Addition of Halogen Compounds to Unsaturated Acids. By A. MICHAEL (*J. pr. Chem.* [2], **40**, 171—179; compare Abstr., 1888, 1054).—Hypochlorous acid combines with acrylic acid, yielding as the principal product β chlorolactic acid, smaller quantities of a liquid acid being at the same time produced. The latter, on reduction, is converted into β-hydroxypropionic acid, and might be regarded as α-β-chlorhydroxypropionic acid; but, according to the "positive-negative" rule, its formation by boiling α-β-dichloropropionic acid with water, and by treating αβ-dihydroxypropionic acid with hydrochloric acid shows that it is probably alloisomeric with β-chlorolactic acid.

The constitution of the products formed by the action of hypochlorous and hydrochloric acids on glycidic acid, the crotonic acids, β-methylglycidic acid, methacrylic acid, and α-methylglycidic acid, is discussed in a similar manner, and the reactions are shown to take place in accordance with the "positive-negative" rule.

Citraconic acid and hypochlorous acid yield the acid COOH·CH(OH)·CClMe·COOH, and the same compound is obtained by boiling α-β-citradichloroglutaric acid with water. With hydrochloric acid, hydroxycitraconic acid gives a chlorhydroxyglutaric acid different from the above, but both, on reduction, are converted into the same α-hydroxyglutaric acid. It follows, therefore, that the relationship between the two is the same as that existing between the corresponding derivatives of butyric acid.

The "positive-negative" rule holds good, therefore, in this case also, and its general application may be stated as follows:—

In organic compounds of the fatty series which contain several hydroxyl-groups, that which is combined with the, relatively, most positive carbon-atom is, for the most part, the first to be displaced by halogens.

When an organic compound contains several symmetrically arranged atoms of the same halogen, that which is combined with the, relatively, most negative carbon-atom is the first to be substituted by another atom or group.

In the addition of halogen and cyanogen acids to oxides of polyvalent organic radicles, the halogen and the cyanogen combine with the, relatively, most positive carbon-atom.

When a reagent combines directly with a halogen-free, unsaturated compound of the fatty series, the most negative constituent combines, at any rate for the most part, with that unsaturated carbon-atom which, according to the "positive-negative" rule, is, relatively, the most positive.

When a halogen acid combines directly with an unsaturated acid of the fatty series, the halogen combines with the, relatively, most positive unsaturated carbon-atom, and with that atom alone.

F. S. K.

Derivatives of Ethyl Acetocyanacetate. By A. HELD (*Bull. Soc Chim.* [3], 1, 306—311; compare Abstr., 1888, 579).—On mixing bromine and ethyl acetocyanacetate, in molecular proportion, they react to form a dibromo-derivative, $CH_2Br·CO·CBr(CN)·COOEt$, which is a viscid, yellowish-red liquid, decomposing on distillation under reduced pressure; it is insoluble in alkaline carbonates and hydroxides.

Chlorine is absorbed by a solution of ethyl acetocyanacetate in chloroform to form a dichlorinated derivative, $C_7H_2Cl_2NO_3$, which is a colourless liquid, of irritating odour, and boiling at 90—105° under a pressure of 20—25 mm. It is insoluble in alkalis, and decomposes spontaneously.

Ethyl ethylcyanacetoacetate, $CH_3·CO·CEt(CN)·COOEt$, is prepared by saturating a solution of ethyl ethylsodacetoacetate in absolute alcohol with cyanogen chloride; water is then added, and the upper layer which separates is distilled under reduced pressure; as thus obtained, it is a colourless liquid of sp. gr. 0·976 at 20°, which boils at

103—105° under a pressure of 25 mm.; it is soluble in alcohol and ether, but is insoluble in water and alkalis. When boiled with potassium hydroxide, normal decomposition into acetic and butyric takes place occurs.

Ethyl methylcyanacetoacetate, $CH_3{\cdot}CO{\cdot}CMe(CN){\cdot}COOEt$.—This compound is prepared similarly to the foregoing ethyl-derivative, substituting ethyl methylsodacetoacetate for ethyl ethylsodacetoacetate. It is a colourless liquid of sp. gr. 0·996 at 20°, and boils at 90—92° under 20 mm. pressure. When boiled with potassium hydroxide, it yields acetic and propionic acids.

The author endeavoured to prepare hydrogen acetocyanacetate by Ceresole's process (Abstr., 1882, 1052), but found that, although ethyl acetocyanacetate formed a well-defined potassium compound, subsequent acidification regenerated the ethyl compound. The last-described ethyl- and methyl-derivatives did not saponify with cold solution of potassium hydroxide, even after several months' shaking, whilst slight elevation of temperature under these conditions determined their complete decomposition: this resistance to hydrolysis the author ascribes to the introduction of the (CN)-group.

T. G. N.

Oxamic Acid. By L. OELKERS (*Ber.*, **22**, 2385).—A question of priority.

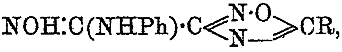
Dithioxamide (Cyanogen Disulphydrate). By J. EPHRAIM (*Ber.*, **22**, 2305—2306).—By the action of cyanogen on an excess of hydrogen sulphide in the presence of water or alcohol, Wöhler obtained a compound of the empirical formula CN,H_2S, to which the name cyanogen disulphydrate (Rubeanwasserstoff) was given. Liebig regarded this substance as dithioxamide, $NH_2{\cdot}CS{\cdot}CS{\cdot}NH_2$, whilst Wollner assigned to it the formula $(SH{\cdot}C{\cdot}NH)_2$. It is best prepared by passing cyanogen into an alcoholic solution of potassium hydrogen sulphide, and afterwards precipitating with hydrochloric acid. It is a brick-red or brownish-red powder, which on treatment in alcoholic solution with hydroxylamine hydrochloride (2 mols.) and the calculated quantity of sodium hydroxide yields Tiemann's diamidoxime, $C_2(NH_2)_2(N{\cdot}OH)_2$, with the evolution of hydrogen sulphide. The investigation is being continued.

W. P. W.

Amidoxime of Oxalic Acid. By F. TIEMANN (*Ber.*, **22**, 1936—1938; compare Fischer, p. 1163).—*Oxalenediamidoxime*,

$$OH{\cdot}N{:}C(NH_2){\cdot}C(NH_2){:}N{\cdot}OH,$$

can be prepared by gradually adding cyanoaniline (100 parts) to a 90 per cent. alcoholic solution (500 parts) of hydroxylamine hydrochloride (50 parts), and treating the resulting red solution in the cold with the calculated quantity of sodium carbonate. The compound thus obtained melts at 195° (uncorr.), and is identical in properties with the oxalenediamidoxime described by Fischer (*loc. cit.*). It is converted into the corresponding azoxime by the action of anhydrides of acids.

Oxaleneanilidoximeamidoxime, $OH{\cdot}N{:}C(NH_2){\cdot}C(NHPh){:}N{\cdot}OH$, is formed, together with aniline and ammonia, when the red solution obtained in the preparation of oxalenediamidoxime is warmed and then sodium carbonate solution gradually added; it crystallises in colourless plates melting at 148°, and shows the properties both of an anilidoxime and of an amidoxime. It is converted into a compound,  $NOH{:}C(NHPh){\cdot}C{<}\begin{matrix}N{\cdot}O\\N\!-\!-\end{matrix}{>}CR$, by anhydrides of acids.

The formation of oxalenediamidoxime in the manner described above seems to show that the constitution of cyanoaniline is probably $NPh{:}C(NH_2){\cdot}C(NH_2){:}NPh$.

Cyanotoluidine behaves with hydroxylamine in the same way as cyanoaniline. F. S. K.

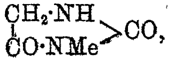
Action of Nitric Acid on Organic Compounds. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, 8, 283—306). —*Methyl nitromalonate*, $NO_2{\cdot}CH(COOMe)_2$, prepared by treating methyl malonate with well-cooled nitric acid (5 parts), is a yellowish liquid heavier than and insoluble in water; it decomposes carbonates with evolution of carbonic anhydride. The *ammonia*-derivative, $NO_2{\cdot}CH(COOMe)_2 + NH_3$, separates from water in yellowish crystals, melts at about 166° with decomposition, and is sparingly soluble in alcohol; it does not give precipitates with solutions of metallic salts.

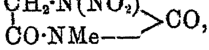
Ethyl nitromalonate, $NO_2{\cdot}CH(COOEt)_2$, prepared in like manner, resembles the methyl-derivative, and forms a crystalline *ammonia* compound, $NO_2{\cdot}CH(COOEt)_2 + NH_3$, which melts at 150° with decomposition.

Methyl nitroisosuccinate, $NO_2{\cdot}CMe(COOMe)_2$, can be obtained, but only in a very impure condition, by dissolving methyl isosuccinate in pure nitric acid; if the crude product is poured into concentrated ammonia the ammonia-derivative of methyl nitropropionate, $NO_2{\cdot}CMeH{\cdot}COOMe + NH_3$, separates from the solution in yellowish nacreous crystals, and the mother-liquors contain methyl carbamate and a crystalline compound, probably isosuccinamide, melting at 206°.

Isosuccinamide, prepared by dissolving methyl isosuccinate in ammonia, crystallises in short, colourless prisms, melts at 206°, and is almost insoluble in ether, and only sparingly soluble in boiling alcohol; it dissolves in nitric acid with evolution of nitrous oxide and carbonic anhydride.

Diacetylethylenediamine is only slowly acted on by pure nitric acid; oxypiperidine and oxymethylpyrrolidine are readily acted on by nitric acid with evolution of nitrous oxide.

Methylhydantoïn,  $\begin{matrix}CH_2{\cdot}NH\\ \vert\\ CO{\cdot}NMe\end{matrix}{>}CO$, prepared by boiling hydantoïn with methyl iodide and methyl alcoholic potash, crystallises from alcohol in colourless prisms, melts at 182°, and is only very sparingly soluble in ether, but readily in alcohol and boiling water.

Nitromethylhydantoïn,  $\begin{matrix}CH_2{\cdot}N(NO_2)\\ \vert\\ CO{\cdot}NMe\!-\!-\end{matrix}{>}CO$, is formed when the preceding compound is dissolved in nitric acid; it crystallises from alcohol in small, shining plates, melts at 168° with decomposition, and is very sparingly soluble in cold water. It is decomposed by hot water, with evolution of carbonic anhydride, yielding the methyl-derivative of nitramidacetamide, which is further decomposed into the methylamide of glycollic acid.

A crystalline compound, probably an isomeride of dinitroacetylenedicarbamide, is formed when acetylenedicarbamide is treated with nitric acid (compare Abstr., 1888, 1179, and this vol., p. 125). It is insoluble in the ordinary solvents, and is decomposed by alkalis and by boiling water.

Methyl acetylcarbamate, NHAc·COOMe, prepared by boiling methyl carbamate with acetic chloride, crystallises from ether in colourless plates melting at 93—94°; it is only very slowly acted on by nitric acid, with evolution of nitrous oxide and carbonic anhydride.

Methyl butyrylcarbamate, $(C_4H_7O)NH\cdot COOMe$, prepared in like manner, crystallises in long, flat needles, melts at 107—108°, and is soluble in alcohol, ether, and water; it is only very slowly acted on by nitric acid, with evolution of nitrous oxide and carbonic anhydride. Methyl carbamate is immediately decomposed by nitric acid.

Dimethyl carboxycarbamate, $NH(COOMe)_2$, prepared by heating methyl carbamate (10 parts) with methyl carbonate (12 parts) and sodium (6 parts), crystallises from water in needles, melts at 134°, and is sparingly soluble in ether. Nitric acid has no action on dimethyl carboxycarbamate, nor on the corresponding ethyl-derivative.

Methylnitramine (compare this vol., p. 492) can be obtained by treating dinitrodimethyloxamide (symm.) with ammonia, separating the oxamide by filtration, and treating the filtrate with dilute sulphuric acid to decompose the ammonium compound of the nitramine. The potassium-derivative crystallises in slender needles, is only sparingly soluble in alcohol, and explodes violently when heated.

Methyl methylnitrocarbamate, $NO_2\cdot NMe\cdot COOMe$, is formed when methyl nitramine is warmed with methyl chlorocarbonate in ethereal solution; it is a colourless liquid, and when treated with anhydrous ammonia in ethereal solution it is converted into methyl carbamate and a solid, unstable compound which decomposes spontaneously, with evolution of ammonia, being converted into methylnitramine.

When ethyl dimethylcarbamate is dissolved in nitric acid, and the product poured on to moist sodium carbonate, ethyl methylnitrocarbamate is produced. If the crude product is treated with anhydrous ammonia in ethereal solution, the ammonium-derivative of methylnitramine is precipitated, and the solution contains ethyl carbamate.

Methyl dimethylcarbamate, $NMe_2\cdot COOMe$, obtained by treating methyl chlorocarbonate with a 33 per cent. aqueous solution of methylamine, is a colourless liquid boiling at 131° (760 mm.). When treated with nitric acid it yields methyl methylnitrocarbamate, which is converted into methyl carbamate and the ammonium compound of methylnitramine by anhydrous ammonia.

Boiling nitric acid has no action on piperidine nitrate, but it acts slowly on acetylpiperidine at the ordinary temperature, yielding a compound, probably nitropiperidine, which is further decomposed by the nitric acid.

Piperylcarbamide crystallises from chloroform in slender needles, melts at 105—106°, and is converted into nitropiperidine when treated with nitric acid at −10°. The *nitrate* forms small crystals and melts at about 67°.

Nitropiperidine is a colourless liquid, boils at 245° (765 mm.) with slight decomposition, and is volatile with steam. It is only sparingly soluble in water, but dissolves in nitric acid at the ordinary temperature, with evolution of carbonic anhydride and oxides of nitrogen, yielding a colourless, crystalline acid, and a yellow, volatile compound.

Ethyl dimethyloxamate is not acted on by nitric acid.

Methyl methyloxamate, NHMe·CO·COOMe, can be prepared by treating methyl oxalate (76 grams) with methylamine (20 grams) in methyl alcoholic solution at the ordinary temperature; the precipitated dimethyloxamide is separated by filtration, the filtrate is evaporated, and the residue is extracted with cold ether to free it from unchanged methyl oxalate. It crystallises from methyl alcohol in short, colourless prisms, melts at 85°, and is very readily soluble in water and methyl alcohol, but only sparingly in ether. It dissolves in nitric acid, but a nitro-compound could not be isolated.

F. S. K.

Influence of Certain Groups on the Behaviour of Organic Compounds with Nitric Acid. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 8, 307—318; compare Abstr., 1888, 1052, 1179).—The hydrogen-atom of the imido-group in compounds of the fatty series reacts with nitric acid when the nitrogen is in direct combination with a carbonyl-, acetyl-, or carboxymethyl-group; in the first two cases, the compound obtained is unstable, in the latter case it is stable. When, however, the negative element (oxygen) accumulates in the neighbourhood of the imido-group, the reaction between the hydrogen of the imido-group and the nitric acid may be entirely prevented.

All compounds containing a C_nH_{2n+1}·CO-group combined with nitrogen give a nitro-compound which is unstable in presence of nitric acid. The compound is stable only when a group sufficiently negative, such as a methoxy-group, is in combination with the carbonyl-radicle, but its stability may be lessened by the presence of other groups or elements.

The hydrogen of an imido-group situated between two carbonyl radicles which are in combination with alkyl-groups, reacts with nitric acid. If, however, a negative element, such as oxygen, is introduced into both the alkyl-groups, the compound does not react with nitric acid; the same effect is produced by a loss of hydrogen accompanied by the formation of a closed chain. F. S. K.

Tetramethylsuccinic Acid. By K. AUWERS and V. MEYER (*Ber.*, 22, 2011—2015; compare Hell, *Ber.*, 10, 2229).—Two acids can be obtained by treating ethyl α-bromisobutyrate with finely-divided silver and hydrolysing the resulting ethereal salts; both have the composition of a dimethylsuccinic acid. The one is readily volatile with steam, melts at about 190°, and when heated alone or with steam it gives out a strong smell very like that of camphor; the ether melts at 95°, is not volatile with steam, and is more readily soluble in water than the isomeric acid. When warmed with acetic chloride, both acids give crystalline products, probably anhydrides; the compound obtained from the acid melting at 190° is exceedingly volatile and has a strong odour of camphor. F. S. K.

Fumaric and Maleic Acids. By V. SEMENOFF (*J. Russ. Chem. Soc.*, 1888, **21**, 537—539).—Monobromomaleïc acid, obtained by the decomposition of dibromosuccinic acid (m. p. 126—128°), was heated in a small sealed tube in amyl alcohol vapour at 132° for eight hours. After cooling and heating again at 132°, part of the acid was found to remain solid at that temperature. On heating again for seven hours, all the acid was found to remain solid at 132°, owing to the change of the monobromomaleïc acid into the isomeric monobromofumaric acid. On treating dibromomaleïc acid in the same manner for 30 hours, no isomeric change took place, but some of the acid was decomposed, with evolution of carbonic anhydride.

Potassium maleate, prepared from the pure acid, was heated at 140—150° for 20 hours in a sealed tube with some water and a few drops of potassium hydroxide solution, and the salt was then decomposed with the theoretical amount of sulphuric acid and the acid extracted with ether; on evaporation, fumaric acid was left. Barium maleate is converted into the fumarate only when heated to above 220°. B. B.

Condensation of Ketonic Acids with Bibasic Acids. By R. FITTIG and G. PARKER (*Ber.*, **22**, 2104—2106; compare this vol., pp. 592 *et seq.*).—When a mixture of pyruvic acid, sodium succinate, and acetic anhydride, in molecular proportion, is heated on a water-bath, the colour rapidly darkens, and after some time carbonic anhydride is evolved and an acid having the composition $C_6H_8O_3$ is formed. This compound occurs together with acetic acid in the distillate obtained on steam-distilling the product of the reaction, and crystallises from water in very large, thin, colourless, transparent prisms, melts at 94°, is volatile at the ordinary temperature, has a very characteristic odour, and is sparingly soluble in cold water. Experiments are in progress having for their object the isolation of the first product of the condensation, which, by the elimination of carbonic anhydride, is converted into the acid $C_6H_8O_3$. W. W.

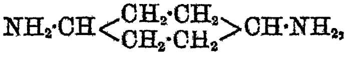
Oxidation of Erucic Acid. By L. URWANTZOFF (*J. Russ. Chem. Soc.*, 1889, **21**, 13—17; and *J. pr. Chem.*, **39**, 334).—To an alkaline solution of erucic acid, potassium permanganate solution was gradually added, and the product of the reaction decomposed with sulphuric acid; in this way *dihydroxybehenic acid*, $C_{22}H_{44}O_4$, was obtained, melting at 127°. This acid, when treated with phosphorus triiodide, gave iodobehenic acid, which yielded behenic acid on reduction with zinc and hydrochloric acid. B. B.

Action of Malic Acid on Ammonium Molybdate. By D. Gernez (*Compt. rend.*, **109**, 151—154).—A solution of 1·1166 gram of lævogyrate malic acid in 12 c.c. of water was mixed with increasing quantities of ammonium molybdate and the rotatory power at 17° determined in a tube 105·7 mm. in length. The rotatory power of the malic acid solution was −0° 12′, and as the proportion of molybdate is gradually increased, the rotatory power increases and attains a maximum at −5° 19′, which is 35 times as great as that of the original acid, and corresponds with a solution containing nine equivalents of malic acid for each equivalent of the molybdate. As the proportion of molybdate is still further increased, the rotatory power diminishes, then changes its sign, and afterwards gradually increases, a distinct break in the rate of change being observed when three equivalents of the acid are present for each equivalent of the salt. With from three to two equivalents of acid per equivalent of molybdate, the increase in rotatory power is proportional to the quantity of molybdate added. The rotatory power reaches its maximum at +72° 48′, which is 364 times that of the original acid, and corresponds with equal equivalents of malic acid and ammonium molybdate. C. H. B.

Oxidation of Ricinoleic Acid. By V. Dieff (*J. Russ. Chem. Soc.*, 1889, 17—24; and *J. pr. Chem.*, **39**, 339).—A mixture of two isomeric trihydroxystearic acids was obtained by the oxidation of ricinoleic acid with alkaline potassium permanganate. B. B.

Succinosuccinic Acid. By A. Baeyer and W. A. Noyes (*Ber.*, **22**, 2168—2178).—Succinosuccinic acid can readily be prepared by the hydrolysis of ethyl dihydroxyterephthalate (4 grams) with 5 per cent. aqueous soda (40 c.c.), and then adding 3 per cent. sodium amalgam (35 grams) to the carefully cooled solution; the reduction is complete in from 8 to 10 minutes, and the acid separates as a pale yellow, pulverulent precipitate on pouring the solution into dilute sulphuric acid cooled with pieces of ice. The yield amounts to 60 per cent. of that theoretically possible. Succinosuccinic acid is soluble to the extent of 1 part in 6600 parts of water at 19·5°, and in solution is gradually oxidised to dihydroxyterephthalic acid on exposure to the air; it slowly decomposes also into carbonic anhydride and succinopropionic acid when allowed to remain in contact with an aqueous liquid (compare Herrmann, Abstr., 1882, 712). When heated for some minutes at 200° until the evolution of carbonic anhydride has ceased, it is converted into paradiketohexamethylene, which may be purified by distillation under reduced pressure and melts at 78° (compare Herrmann, *loc. cit.*).

On treatment with hydroxylamine, diketohexamethylene yields a *dioxime*, $C_6H_8(N{\cdot}OH)_2$, which forms small, colourless crystals, melts at 192° when slowly and at 200° when rapidly heated, and is moderately soluble in water. *Paradiamidohexamethylene*,



$$NH_2{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}NH_2,$$

is obtained from the dioxime by reduction with sodium and alcohol.

It is an oil with a faint ammoniacal odour, and resembles Bamberger's "alicyclic" tetrahydronaphthylamines in its properties. The *hydrochloride* is crystalline, and is readily soluble in water but very sparingly soluble in alcohol; the *sulphate* crystallises in needles; the *carbonate* and *nitrite* are also described. The *platinochloride*, $C_6H_{10}(NH_2)_2,H_2PtCl_6$, crystallises in sparingly soluble, yellow scales, and decomposes without previous fusion when heated. The *diacetyl-derivative*, $C_6H_{10}(NHAc)_2$, crystallises in needles, melts at 310°, and is readily soluble in hot water.

Diketohexamethylenediphenylhydrazone, $C_6H_8(N_2HPh)_2$, is prepared by adding a solution of phenylhydrazine acetate to an aqueous solution of the diketone; a white precipitate melting at about 125° is first formed, and this, when crystallised from alcohol, yields small, yellow prisms melting at 150—151°. It is a feeble base and forms very unstable salts; the *hydrochloride*, $C_6H_8(N_2HPh)_2,2HCl$, for example, rapidly loses hydrogen chloride on exposure to the air. On reduction with sodium and ethyl alcohol, it is converted into *paradiphenylhydrazohexamethylene*, $C_6H_{10}(NH{\cdot}NHPh)_2$, which seems to exist in two forms—a solid and an oil. Of these, the former, possibly the "fumaroïd" modification, is crystalline, melts at 147—148°, is insoluble in water and moderately soluble in alcohol, and forms a *hydrochloride*, crystallising in lustrous, silvery-white scales sparingly soluble in water and alcohol, whilst the latter, possibly the "maleïnoïd" form, yields a crystalline *oxalate* having the composition $C_6H_{10}(NH{\cdot}NHPh)_2,C_2H_2O_4 + H_2O$.

When a mixture of diketohexamethylene and potassium cyanide is treated drop by drop with hydrochloric acid and allowed to remain for some time, the *cyanhydrin*, $C_6H_8(CN)_2(OH)_2$, is obtained. This melts at 180° with decomposition, is easily soluble in hot and very sparingly soluble in cold water, dissolves readily in alcohol and ether, and on hydrolysis with concentrated hydrochloric acid is converted into an acid, probably α-dihydroxyhexahydroterephthalic acid. The *barium* salt, $C_6H_8(OH)_2(COO)_2Ba + 3\frac{1}{2}H_2O$, crystallises partly in short, thick prisms, and partly in concentrically grouped needles, and is very sparingly soluble in water.

Diketohexamethylene does not form a diimide when treated with ammonium acetate by Knorr's method, but is converted into a red, amorphous substance, which dissolves in alcohol with a greenish-yellow fluorescence, and is in all probability a condensation compound. Nor does it seem to form a glycol, since the sweet syrup obtained when it is reduced with sodium amalgam is neither crystallisable nor volatile, and does not form crystallisable or distillable compounds on treatment with acetic or benzoic chloride. It is not attacked when heated with acetic anhydride for six hours at 155—165°, and does not form definite products either when heated with acetic chloride for six hours at 110—120°, or when the white precipitate obtained on adding sodium ethoxide to its ethereal solution is treated with acetic chloride. These negative results lead the authors to conclude that diketohexamethylene has only a very slight tendency to pass into the hydroxy-form, and must therefore be removed from the list of tautomeric compounds. W. P. W.

Dihydroxytartaric Acid. By W. L. MILLER (*Ber.*, **22**, 2015—2016).—*Dihydroxytartaric acid*, $COOH{\cdot}C(OH)_2{\cdot}C(OH)_2{\cdot}COOH$, can be obtained by decomposing the sodium salt with anhydrous hydrogen chloride, the salt being covered with perfectly dry ether. It is a colourless crystalline substance, melts at 98° with decomposition, and is very readily soluble in water; it yields an orange osazone when warmed with phenylhydrazine hydrochloride. F. S. K.

Reduction of Acids of the Sugar-group. By E. FISCHER (*Ber.*, **22**, 2204—2205).—When a cold aqueous solution of gluconic acid is treated with sodium amalgam and neutralised from time to time with sulphuric acid, it soon acquires the power of reducing Fehling's solution, owing to the production in considerable quantity of a sugar which yields pure phenylglucosazone with phenylhydrazine, and is in all probability dextrose.

The acid isomeric with gluconic acid which is formed by the action of bromine in aqueous solution on mannose (this vol., p. 482) yields a well-crystallised lactone, and this, on reduction with sodium amalgam in a solution kept as nearly neutral as possible throughout the reaction, is converted into mannose, the yield at the end of an hour amounting to 40 per cent. of that theoretically possible. Prolonged action of the reducing agent brings about the formation of mannitol and consequent disappearance of the sugar.

Arabinosecarboxylic, mannosecarboxylic, and rhamnosecarboxylic acids react similarly with sodium amalgam, and bibasic acids of this group are also reduced under like conditions; thus saccharic acid yields a strongly reducing compound possibly identical with glycuronic acid. Glyceric, malic, and tartaric acids, however, are not reduced to aldehydes on treatment with sodium amalgam, and the capacity of acids for reduction by this method seems to be connected with their tendency to form lactones.

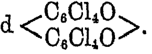
These results afford an explanation of the action of sodium amalgam on the double lactone of metasaccharic acid whereby mannitol is produced (Kiliani, Abstr., 1888, 46), since aldehydes most probably form intermediate products of the reaction and would escape detection from the fact that the double lactone reduces Fehling's solution.

Scheibler (Abstr., 1884, 574) found that saccharin is readily reduced by sodium amalgam in alkaline solution; the author has examined the product formed when the reduction is effected in a solution kept as nearly neutral as possible, and finds that a sugar possibly isomeric with rhamnose is formed in considerable quantity. The investigation is being continued. W. P. W.

Perchlorination of Phenol. By L. HUGOUNENQ (*Compt. rend.*, **109**, 309—310).—The prolonged action of chlorine on pentachlorophenol is known to yield the derivative C_6Cl_6O, which can also be obtained by the action of chlorine on pentachloraniline, and by the action of the gas at 110° on anisoïl mixed with antimony pentachloride.

After washing with water and drying, this compound crystallises in colourless or slightly yellowish, quadratic prisms, which melt at 107—108°, are insoluble in water, and only slightly soluble in alcohol, but dissolve readily in benzene and in chloroform. When treated with aqueous potash, it yields potassium hypochlorite and pentachlorophenol. It is but slightly attacked by sodium in presence of benzene, and is not affected by acetic chloride, benzene in presence of aluminium chloride, or zinc powder at 110°. Aniline, when added to the cold alcoholic solution, yields a beautiful red colouring matter.

When heated somewhat above 200°, the compound C_6Cl_6O gives off chlorine, and after heating for several hours at 210—220° a solid product is obtained consisting of a mixture of Julin's chloride, C_6Cl_6, and an easily crystallisable substance which melts at 323°, is insoluble in ordinary solvents, and is only slightly volatile at 440°. This substance is identical with the *perchlorodioxydiphenylene* $(C_6Cl_4O)_2$ of Merz and Weith. It is very stable, but if heated strongly with antimony pentachloride for several hours, it yields chloranil and hexachlorobenzene.

The complete series of reactions is as follows:—Pentachlorophenol yields the compound $C_6Cl_5{\cdot}OCl$, which at 210° loses chlorine, and is converted into hexachlorobenzene and the compound  $<\substack{C_6Cl_4O\\ C_6Cl_4O}>$. The latter in presence of chlorine (derived from the antimony chloride) yields hexachlorobenzene and chloranil. Chloranil in contact with phosphorus pentachloride yields hexachlorobenzene. These reactions explain the very frequent formation of hexachlorobenzene during the action of chlorinating agents. C. H. B.

New Class of Iodated Phenols. By J. MESSINGER and G. VORTMANN (*Ber.*, **22**, 2312—2322).—When a solution of phenol (1 mol.) in aqueous potash (4 mols.) is heated at 50—60° with an excess of iodine (4 mols.) dissolved in aqueous potassium iodide, a dark violet-red precipitate is obtained having the composition $C_6H_3I_3O$. This compound is not crystallisable, is without odour, and is insoluble in water and dilute acids, but readily soluble in alcohol, ether, benzene, and chloroform. When heated, it sinters at 116°, melts at about 157° to a dark-brown mass with decomposition, and at higher temperatures loses iodine. On distillation with steam, iodine is liberated, and the distillate, on keeping, gives a few white needles which melt at 138—140° and probably consist of diiodophenol. When boiled with aqueous potash, it is almost completely dissolved, and the solution on acidification gives a white precipitate of the known triiodophenol (m. p. = 154—156°), the filtrate being free from iodine. On reduction with sodium amalgam, or with zinc-dust in alkaline solution, it is converted into phenol. The authors are inclined to regard it as an *iodoxydiiodobenzene*, $C_6H_3I_2{\cdot}OI$.

The cresols in alkaline solution react in like manner with iodine, forming amorphous compounds insoluble in water, dilute acids, and boiling aqueous potash, but readily soluble in alcohol and ether. The compound from orthocresol is a brown *diiodo*-derivative, which sinters at 115° and melts at about 150°; that from metacresol is a brownish-yellow *triiodo*-derivative, and melts at above 200°; whilst that from paracresol consists of a mixture of a *diiodo-* and *triiodo*-derivative, is brownish-yellow in colour, sinters at 74°, and melts at 90°.

When thymol (1 mol.) dissolved in aqueous potash (4 mols.) is treated with an excess of iodine dissolved in aqueous potassium iodide, a brownish-red, amorphous compound is obtained having the composition of a diiodothymol. The same compound is also formed by the action of iodine on the alkaline solution of Willgerodt's iodothymol (Abstr., 1888, 940; this vol, p. 697). It melts at about 110° with the liberation of iodine, is insoluble in water, sparingly soluble in alcohol, and readily soluble in ether and chloroform, retains its colour for many months, and when preserved in a dry state in the dark, although it decomposes in the course of a few hours on exposure to light, or when kept in a moist state in a closed flask, with the liberation of iodine and formation of a yellow compound. This yellow substance is also an iodo-derivative, and is formed when the brownish-red compound is boiled with water, aqueous alkalis, or aqueous solutions of sulphurous anhydride, sodium sulphite, or sodium thiosulphate. It is without odour, melts at 165°, and dissolves in small quantity in boiling aqueous potash, forming a solution which, on treatment with iodine, yields a precipitate of the red compound; on reduction with either sodium amalgam or zinc-dust in alkaline solution, it is converted into a substance agreeing in its properties and melting point (135°) with a specimen of so-called dithymol prepared according to Dianin's method by the action of a solution of iron alum on thymol (*J. Russ. Chem. Soc.*, **14**, 135). Dianin's compound does not melt at 165·5°, as stated by him, but at 135°, and on analysis gives numbers agreeing fairly well with those required for a hydroxydithymol. The possible formulæ for the red and yellow iodo-derivatives are discussed in the paper.

Potassium iodoxydiiodoresorcinol, $OK{\cdot}C_6H_2I_2{\cdot}OI$, is obtained as a violet-red precipitate by treating an alkaline solution of resorcinol with iodine dissolved in aqueous potassium iodide. When digested with a dilute acid, it yields a red precipitate of *iodoxydiiodoresorcinol*, which dissolves readily in aqueous alkalis and in alcohol and ether.

Guaiacol. under similar conditions, forms a coffee-brown precipitate of an iodo-derivative which sinters at 100°, melts at 125—130°, dissolves in hot aqueous potash, and loses iodine in small quantity when boiled with water.

The hydroxybenzoic acids in alkaline solution yield coloured iodo-derivatives when treated with iodine. The *diiodo*-derivative prepared from salicylic acid is a red powder, and dissolves in boiling aqueous potash, forming a solution from which acids precipitate a white, crystalline compound melting at 165° and probably identical with the known diiodosalicylic acid. Metahydroxybenzoic acid yields a coffee-brown *tetriodo*-derivative, $COOH{\cdot}C_6HI_3{\cdot}OI$, whilst the para-acid forms a yellow iodo-compound.

α- and β-naphthol, under like conditions, are converted into coloured iodo-derivatives; that from α-naphthol is dark-violet in colour, whilst the β-naphthol-compound is yellowish-green, sinters at 78°, and melts at 100°.

W. P. W.

Dyes derived from Benzidine. By A. Colson (*Bull. Soc. Chim.* [3], 1, 347—348).—To quinol (8 grams), sufficient alcoholic potash is added to form the compound $C_6H_4(OK)_2$, and after the addition of an equivalent amount of benzyl chloride, the mixture is boiled for two hours in a flask with a reflux condenser, the alcohol is then distilled off, the residue after washing with water and ether yields a white substance, quinol dibenzyl ether, $C_6H_4(O\cdot CH_2Ph)_2$, which is insoluble in these re-agents: 10 grams of this compound is dissolved in glacial acetic acid (10—12 parts), the solution is cooled to 30°, and, after addition of nitric acid (½ vol.), the mixture is warmed until a limpid liquid is obtained; this, on cooling, deposits yellow crystals of the nitro-derivative $C_{20}H_{17}O_2\cdot NO_2$, which melts at 78°, and is soluble in dry ether and boiling alcohol.

By reduction of this nitro-derivative with zinc in alkaline solution, a yellow compound melting at 140°, and a small amount of a base soluble in alcohol, are obtained; with dilute hydrochloric acid, the latter forms benzidine hydrochloride which yields a tetrazo-derivative, $Cl\cdot N_2\cdot C_{20}H_{17}O_2\cdot C_{20}H_{17}O_2\cdot N_2Cl$; this combines with naphtholsulphonic acid, salicylic acid, and other phenols to form colours which dye cotton in an alkaline bath. T. G. N.

Benzoyl-compounds with Alcohols, Phenols, and Sugars. By Z. H. Skraup (*Monatsh.*, **10**, 389—400; compare Abstr., 1887, 228, and 1888, 1296).—*Tribenzoylpyrogallol*, $C_6H_3(OBz)_3$, is formed when pyrogallol is mixed with a 10 per cent. solution of sodium hydroxide and benzoic chloride in the ratio of 7 mols. of soda and 5 mols. of benzoic chloride to each hydroxyl-radicle in the pyrogallol, the operation being conducted in a flask filled with coal-gas. It crystallises from alcohol in beautiful, colourless prisms melting at 89—90°, and is identical with the compound obtained in an impure condition by Nachbaur (*Annalen*, **107**, 245), and thought by him to be a dibenzoylpyrogallol. A compound containing fewer benzoyl-groups and melting at 129—131·5° is obtained simultaneously. Under similar circumstances, phloroglucinol appears to give two isomeric *dibenzoylphloroglucinols*, of which one melts at 163—165°, and is readily soluble in benzene; the other melts at 191—195°, and is dissolved with difficulty by that solvent. The benzoyl-compounds derived from phenol and resorcinol have been previously described and are well known.

Alcohols containing several hydroxyl-groups readily react with benzoic chloride in presence of potash, with formation of resinous products, insoluble in water and in light petroleum, but readily soluble in and crystallising from hot benzene. *Tribenzoylglycerol*, $C_3H_5(OBz)_3$, when pure, crystallises in colourless prisms melting at 76—76·5°. *Tetrabenzoylerythrite*, $C_4H_6(OBz)_4$, crystallises from acetic acid in minute crystals, and melts at 186·5—187°. *Pentabenzoylmannitol*, $C_6H_9O_6Bz_5$, appears to exist in two isomeric modifications, one of which melts at 70°, the other at 80°. *Hexabenzoylmannitol*, $C_6H_8(OBz)_6$, melts at 149°.

Pentabenzoyldextrose, $C_6H_7O_6Bz_5$, is obtained by the action of benzoic chloride and potash on dextrose. It crystallises from alcohol and melts at 179°. *Pentabenzoylgalactose* crystallises in microscopic needles melting at 165°. *Tetrabenzoyllevulose* melts at 85°. Cane-sugar and milk-sugar give hexabenzoyl-derivatives melting at 109° and 130—136° respectively. *Pentabenzoylmaltose* melts at 110—115°.

G. T. M.

Hexamethylphloroglucinol. By O. Margulies (*Monatsh.*, **10**, 459—463; compare Abstr., 1888, 822).—Having observed its resemblance to the hexethylphloroglucinol described by Herzig and Zeisel, the author now finds, by careful analysis, that the substance obtained by him in an impure condition on treating phloroglucinol with potash and methyl iodide (this vol., p. 497) is not pentamethylphloroglucinol but *hexamethylphloroglucinol*. This conclusion is confirmed by the fact that on treatment with a saturated solution of hydrogen iodide in sealed tubes at 200°, the compound breaks up into a mixture of diisopropylmethane, $CHMe_2·CH_2·CHMe_2$, and isobutyric acid, $CHMe_2·COOH$. G. T. M.

Catecholphthaleïn. By A. Baeyer and E. Kochendoerfer (*Ber.*, **22**, 2196—2200).—*Catecholphthaleïn*, $CO{<}\substack{C_6H_4\\ O\text{—}}{>}C[C_6H_3(OH)_2]_2$, is obtained when phthalic anhydride (3 parts) is heated with catechol (2 parts) and zinc chloride (3 parts) in an oil-bath at 140—150° for 3 to 4 hours; concentrated sulphuric acid and stannic chloride cannot be used to bring about the condensation, since they decompose the phthaleïn as rapidly as it is formed. The melt, after cooling, is extracted with water, and the solution treated with very dilute aqueous soda until it becomes light-blue, then extracted with ether, the ethereal solution evaporated, and the residue dissolved in water, boiled with charcoal, again extracted with ether, and the ethereal solution evaporated to dryness. It is a yellow, uncrystallisable substance, and is readily soluble in alcohol, and moderately soluble in cold water. Alkalis dissolve it with a pure blue, alkaline carbonates with a violet, and concentrated sulphuric acid with a red colour. It dyes cotton mordanted with iron oxide and alumina, and the shades vary from blue to black, but they are not fast. On reduction with zinc dust and aqueous soda, it yields a phthalin resembling phenolphthalin in properties. The *tetrabenzoyl*-derivative, $C_{48}H_{30}O_{10}$, is formed by shaking an excess of benzoic chloride with a solution of the phthaleïn in about 40 parts of 10 per cent. aqueous soda until all odour of the chloride has disappeared. It crystallises in faintly coloured needles, melts at 201—202°, and is soluble in alcohol, ether, and ethyl acetate. The *tetranitrobenzoyl*-derivative, $C_{48}H_{26}O_{18}N_4$, prepared in like manner from metanitrobenzoic chloride and the phthaleïn, crystallises from alcohol and ethyl acetate in small, colourless needles.

Guaiacolphthaleïn is obtained by heating phthalic anhydride (15 grams) with guaiacol (25 grams) and stannic chloride (30 grams) at 110—115° for 3—4 hours. It is an uncrystallisable substance, and dissolves in solutions of caustic alkalis and alkaline carbonates with a violet, and in concentrated sulphuric acid with a cherry-red colour. The *acetyl*-compound is a thick, brown, uncrystallisable oil;

the *dibenzoyl*-derivative, $C_{36}H_{28}O_8$, crystallises in small, pale-yellow, cubical forms, is soluble in alcohol, and readily undergoes hydrolysis when treated with alcoholic potash. W. P. W.

Tetranitrophenylmethylnitramine and its Conversion into Metaphenylenediamine-derivatives. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, 8, 273—282).—*Tetranitrophenylmethylnitramine*, $C_6H(NO_2)_4{\cdot}NMe{\cdot}NO_2$ [= 2 : 3 : 4 : 6 : 1]. is obtained when either of the trinitrodimethylanilines melting at 196° and 154° respectively is dissolved in fuming nitric acid, and the solution warmed for some time. It crystallises in small, yellowish needles, melts at 145—146°, and when boiled with water is converted into trinitromethylnitramidophenol. Trinitromethylnitramidophenol (compare Abstr., 1888, 1079) can also be prepared by boiling either of the trinitrodimethylanilines for a long time with fuming nitric acid or by boiling dinitrodimethylamidophenol with nitric acid of sp. gr. 1·5. It is a yellow, crystalline compound, melts at 187—188° with decomposition, and is soluble in alcohol, benzene, and water; it is decomposed by hot potash with evolution of methylamine. The *potassium*-derivative forms small, anhydrous crystals, is soluble in water and alcohol, and explodes when heated.

Methyl trinitromethylnitramidophenyl ether, [$NMeNO_2 : OMe : (NO_2)_3$ = 1 : 3 : 2 : 4 : 6], prepared by boiling the nitramine with methyl alcohol, forms yellowish crystals, melts at 99°, and is not acted on by hot nitric acid. The corresponding *ethyl-derivative* melts at 98°, and resembles the preceding compound.

Trinitromethamidomethylnitramidobenzene,

$$[NMeNO_2 : NHMe(NO_2)_3 = 1 : 3 : 2 : 4 : 6],$$

prepared by treating tetranitrophenylmethylnitramine or ethyl trinitromethylnitramidophenyl ether with a 33 per cent. aqueous solution of methylamine in the cold, separates from acetic acid in small, yellow crystals, melts at 192°, and is converted into trinitrometaphenylenedimethyldinitramine (m. p. 205°) by nitric acid of sp. gr. 1·5. When tetranitrophenylmethylnitramine is warmed with an aqueous solution of methylamine, trinitrodimethylmetaphenylenediamine is formed. Tetranitrophenylmethylnitramine also reacts readily with aniline, dimethylaniline, and with ammonia. F. S. K.

Oxidation of Aromatic Orthodiamines. By F. KEHRMANN (*Ber.*, 22, 1983—1985).—*Diamidotolazinedicarboxylic acid*, $C_{16}H_{14}N_4O_4$, is precipitated as a brownish-yellow, semi-crystalline compound when ferric chloride is added to a hydrochloric acid solution of diamidoparatoluic acid, [$COOH : Me : (NH_2)_2$ = 1 : 4 : 2 : 3]. It is insoluble in most of the ordinary solvents, but it dissolves in concentrated hydrochloric acid with a blood-red coloration, and in dilute alkalis with a yellowish-red coloration. Its constitution is either

$$\overset{1}{\mathrm{COOH}}{\cdot}\mathrm{C_6H_2}\overset{4}{\mathrm{Me}}{\cdot}\mathrm{N_2}{\cdot}\mathrm{C_6}\overset{4}{\mathrm{Me}}\mathrm{(NH_2)_2}{\cdot}\overset{1}{\mathrm{COOH}}\text{ or}$$

$$\overset{1}{\mathrm{COOH}}{\cdot}\mathrm{C_6H_2}\overset{4}{\mathrm{Me}}{\cdot}\mathrm{N_2}{\cdot}\mathrm{C_6}\overset{1}{\mathrm{Me}}\mathrm{(NH_2)_2}{\cdot}\overset{4}{\mathrm{COOH}},$$

and the phenazine-derivative of orthophenylenediamine prepared by Fischer and Hepp (this vol., p. 499) is probably analogously constituted.
F. S. K.

Conversion of Phenylazoresorcinol Ethers into Hydroxyquinol-derivatives. By J. Bechhold (*Ber.*, 22, 2374—2384).—*Paraphenylazoresorcinol methyl ether*, $NPh{:}N{\cdot}C_6H_3(OH)(OMe)$, is obtained by methylating para-phenylazoresorcinol. It crystallises from alcohol in orange scales, and is soluble in ether and dilute alkali. No aceto-derivatives could be isolated. *Paraphenylazoresorcinyl dimethyl ether*, $NPh{:}N{\cdot}C_6H_3(OMe)_2$, was obtained by further methylating the mono-ether. It is soluble in alcohol and ether, insoluble in water, and melts at 92°. It forms glistening, red crystals of the monosymmetric system showing the axial relations $a : b : c = 0{\cdot}9978 : 1 : 0{\cdot}6169$, $\beta = 68°34'$.

Paramidoresorcinol dimethyl ether, $NH_2{\cdot}C_6H_3(OMe)_2$, is obtained by the action of stannous chloride on an alcoholic solution of the azo-ether. It forms a slightly coloured mass of small crystals, is soluble in alcohol, ether, and benzene, sparingly so in water, and volatile in steam. It melts at 39—40°. With bleaching powder, it gives a cherry-red, with ferric chloride a green, and with furfurol a yellow coloration. Its *hydrochloride* forms small crystals and sublimes at 100—110° in snow-white needles. The *acetyl-derivative*, $NHAc{\cdot}C_6H_3(OMe)_2$, forms transparent crystals, soluble in alcohol and melting at 115—116°. The *benzoyl-derivative*, $NHBz{\cdot}C_6H_3(OMe)_2$, on sublimation, forms white needles, soluble in boiling alcohol and melting at 173°. The *thiocarbamide* $CS[NH{\cdot}C_6H_3(OMe)_2]_2$, forms a white mass, insoluble in alkalis and melting at 159—160°. The *thiocarbimide*, $CSN{\cdot}C_6H_3(OMe)_2$, formed together with the thiocarbamide by the action of potash and carbon bisulphide on the azo-compound, forms yellow crystals melting at 57°. When the hydrochloride of the azo-base or the amido-ether is oxidised with chromic acid, methoxyquinone, $C_6H_3O_2(OMe)[O : OMe : O = 1 : 3 : 4]$, is formed. This crystallises in yellow needles, melts at 140°, and is identical with that obtained by Schweizer (*Inaug. Dissert., Berlin*, 1888), by the oxidation of orthanisidine. No phenylhydrazine-derivative of the quinone could be obtained.

Paramidoresorcinol methyl ether, $NH_2{\cdot}C_6H_3(OMe){\cdot}OH$, was obtained by the reduction of the azo-mono-ether. It crystallises from benzene in needles melting at about 137—138°, but was not obtained quite pure, as it oxidises so readily when exposed to air. When this amido-compound is heated with benzoic chloride, benzoic acid is among the products of the reaction, and the water for its formation being necessarily furnished by the amide renders it probable that the amido- and hydroxyl-groups are in the ortho-position to one another, and this agrees with the results of Will and Pukall (Abstr., 1887, 660).

From the mother liquors of the para-compound *orthophenylazoresorcinyl dimethyl ether* was isolated. It crystallises from alcohol in orange needles, melts at 96—97°, and is not attacked by cold, concentrated nitric acid.
L. T. T.

Action of Stannous Chloride on Salts of Diazohydrocarbons, and some Reactions of Diazoimidohydrocarbons.

By C. Culman and K. Gasiorowski (*J. pr. Chem.* [2], **40**, 97—120).—When a concentrated solution of diazobenzene chloride (1 mol. proportion = 100 grams of aniline) is treated with a cold, saturated solution of stannous chloride ($\frac{1}{2}$ mol. proportion) and, after keeping for 12 hours in the cold, distilled with steam, benzene (6—6·5 grams), chlorobenzene (13—15 grams), diphenyl (2—2·3 grams), phenol (9—10 grams), and diazobenzeneimide (25—26 grams) are obtained, and aniline (26 grams) remains in the acid solution. When the solution employed is much more dilute, other conditions remaining the same, the products are the same and their respective quantities are the same, excepting that of diazobenzeneimide, which falls to 19—20 grams. When the stannous chloride is added in the solid state, other conditions remaining the same, the products are benzene (11 grams), chlorobenzene (12 grams), diphenyl (2·5 grams), phenol (9 grams), and diazobenzeneimide (14 grams). When a concentrated solution of stannous chloride (1 mol.) is employed, other conditions remaining the same, the products are benzene (13—14 grams), chlorobenzene (2—3 grams), phenol 4—5 grams), diazobenzeneimide (18—19 grams), and aniline (27·5 grams). When a very dilute solution of diazobenzene chloride (1 mol. = 100 grams of aniline) is treated with solid stannous chloride (3 mols.), benzene (34—36 grams), diphenyl (4 grams), and a solid, grey, basic substance are formed.

Diazobenzene sulphate (1 mol. = 100 grams of aniline), in presence of excess of sulphuric acid, is decomposed by stannous chloride ($\frac{1}{2}$ mol.), yielding benzene (6—7 grams), diazobenzeneimide (24—25·5 grams), phenol (22—25 grams), aniline (39 grams), and small quantities of chlorobenzene. Under the same conditions, but employing only the calculated quantity of sulphuric acid, benzene (6 grams), phenol (20 grams), and diazobenzeneimide (23 grams) are obtained.

When a dilute solution of diazobenzene formate (1 mol. = 100 grams of aniline) and excess of formic acid is treated with stannous chloride ($\frac{1}{2}$ mol.), benzene (12—13 grams), chlorobenzene (2—3 grams), diphenyl (8—9 grams), and diazobenzeneimide (8—9 grams) are obtained; in more concentrated solutions the products are benzene (14 grams), chlorobenzene (2 grams), diphenyl (9·6 grams), and diazobenzeneimide (7 grams).

When a solution of diazobenzene chloride (1 mol. = 100 grams of aniline) is mixed with excess of soda and then treated with stannous chloride ($\frac{1}{2}$ mol.), benzene (9 grams), phenol (45 grams), and diazobenzeneimide (10 grams) are formed; the products are the same when soda, just sufficient to make the solution alkaline, is employed, but the yield of phenol (50 grams) is somewhat larger.

Orthodiazotoluene sulphate (1 mol. = 100 grams of orthotoluidine) when treated with a solution of stannous chloride ($\frac{1}{2}$ mol.), yields toluene and chlorotoluene (together 9—11 grams), diazotolueneimide (20—21 grams), orthocresol (12—13 grams), orthotoluidine (26 grams), and resinous products. When orthodiazotoluene chloride is employed, the products are toluene (6 grams), chlorotoluene (14 grams), diazotolueneimide (19 grams), and cresol (10 grams).

Paradiazotoluene sulphate when treated in like manner yields toluene and chlorotoluene (together 10 grams), diazotolueneimide (19 grams), and cresol (12 grams).

β-Diazonaphthalene sulphate (= 100 grams naphthylamine) under the same conditions yields β-diazonaphthaleneimide (10—11 grams), naphthalene (11—12 grams), β-naphthol, and resinous products.

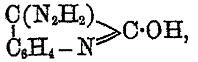
Diazoisobutylbenzene (= 50 grams isobutylamidobenzene), when treated with stannous chloride (½ mol.) in like manner, is decomposed into isobutylbenzene (10—11 grams), isobutylphenol (26—27 grams), and isobutylamidobenzene (6 grams).

Symmetrical tribromaniline (m. p. 119—120°) is formed, with evolution of nitrogen and hydrogen bromide, when bromine in excess is gradually added to well-cooled diazobenzeneimide. Tribromo-orthotoluidine (m. p. 105—107) and tribromoparatoluidine (m. p. 112°) are obtained when the corresponding diazotolueneimides are treated in like manner.

Paranitrodiazobenzeneimide (m. p. 71°) is formed when nitric acid of sp. gr. 1·4 (2 parts) is gradually added to well-cooled diazobenzeneimide; the yield of the pure compound is 30 per cent. of the diazoimide, but when nitric acid of sp. gr. 1·4 (2 parts) and concentrated sulphuric acid (1 part) are used the yield is about 37 per cent.

F. S. K.

Substitution of the Azo-group for Ketonic Oxygen. By T. Curtius (*Ber.*, 22, 2161—2164).—When diketones or compounds which contain a ketonic group in a ring of carbon or carbon and nitrogen atoms are treated with hydrazine hydrate, a substitution of the hydrazo-group, N_2H_2, for the oxygen of the ketonic group takes place; thus benzil yields hydrazobenzil, $COPh\cdot CPh(N_2H_2)$, and dihydrazobenzil, $N_2H_2{:}CPh\cdot CPh{:}N_2H_2$, and isatin forms hydrazoisatin,



$$\begin{matrix} C(N_2H_2) \\ | \\ C_6H_4-N \end{matrix}\!\!>\!C\cdot OH,$$

under these conditions. These compounds are almost colourless, and most probably contain the radicle NH·NH and not $N\cdot NH_2$, inasmuch as on distillation nitrogen is eliminated; thus hydrazobenzil and hydrazoisatin on distillation yield respectively benzyl phenyl ketone and pseudoxindole or oxindole. The hydrazo-compounds when shaken with mercuric oxide in a cold benzene solution are oxidised to ketazo-derivatives in which the ketonic oxygen-atom is replaced by the azo-group.

Ketazodiphenyl ketone, $COPh\cdot CPh{<}\overset{N}{\underset{N}{\|}}$, is readily obtained in theoretical quantity by shaking a cold benzene solution of hydrazobenzil with mercuric oxide. During the reaction, the colourless solution of the hydrazo-compound changes to deep orange-red, and after filtering from the mercury and evaporating the benzene solution in the cold, a golden-yellow residue is obtained, which crystallises from ether in large, transparent, rectangular, brick-red tables, melts at 63° with decomposition, explodes when rapidly heated above its melting point, and, as determined by Raoult's method in a benzene solution, has a molecular weight of 198·5—213. Ketazodiphenyl ketone effervesces when treated with acids, decomposes with the elimination of nitrogen and decolorisation when boiled with water, and on treating its cold ethereal solution with iodine it gives off gas violently, thus resembling the diazo-fatty compounds.

Dihydrazo-derivatives such as dihydrazobenzil or dihydrazodiacetyl do not yield stable diketazo-compounds, but the whole of their nitrogen is eliminated when their solutions in cold benzene are shaken with mercuric oxide; thus, on treatment with mercuric oxide, dihydrazobenzil is decomposed with the formation of tolane.

W. P. W.

Sodium Phenylhydrazine. By A. MICHAELIS (*Annalen*, **252**, 266—270).—*Sodium phenylhydrazine* (Abstr., 1886, 1025) is most conveniently prepared by the following process. A retort half filled with phenylhydrazine (100 grams) is heated at 130—140° in a paraffin bath; clean sodium (13·5 grams), which has been scraped and cut up under petroleum, is added in small portions at a time. Dry hydrogen is now passed through the retort, and the temperature is raised to 160°. The excess of phenylhydrazine, together with the aniline formed during the reaction, are removed by heating the contents of the retort at 180°, under a reduced pressure of 200 mm. On cooling, the retort is broken, and the product is dropped into absolute ether or benzene.

W. C. W.

Action of Alkyl Bromides and of Benzyl Chloride on Sodium Phenylhydrazine. Preparation of Unsymmetrical Secondary Phenylhydrazines. By B. PHILIPS (*Annalen*. **252**, 270—300).—Unsymmetrical or α-ethylphenylhydrazine, $NEtPh{\cdot}NH_2$, formed by the action of ethyl bromide on sodium phenylhydrazine in presence of benzene, has been previously described by E. Fischer, who obtained it by the reduction of phenylethylnitrosamine. Benzaldehyde acts on this compound forming *benzylidenethylphenylhydrazine*,

$$NEtPh{\cdot}N{:}CHPh;$$

the product only separates out when the mixture is cooled down below 0° for some hours; on recrystallisation from alcohol, the pure compound is obtained in needles; it melts at 49°. *Diphenylethylthiosemicarbazide*, $NEtPh{\cdot}NH{\cdot}CS{\cdot}NHPh$, is deposited in colourless crystals when an alcoholic solution of equivalent quantities of α-ethylphenylhydrazine and phenylthiocarbimide is warmed for a few minutes and then allowed to cool. This compound melts at 149° and is insoluble in ether and only sparingly soluble in hot alcohol.

Diethylphenylazonium iodide, $NEt_2PhI{\cdot}NH_2$, is formed by the action of ethyl iodide on α-ethylphenylhydrazine; and is deposited as a white crystalline powder, when ether is added to the crude product; it melts at 145° and closely resembles the corresponding chloride and bromide which have already been described by E. Fischer (Abstr., 1878, 302).

Diethyldibenzyldiamidotriphenylmethane appears to be formed when a mixture of benzaldehyde, benzyl chloride, and a solution of α-ethylphenylhydrazine in benzene is heated at 180° in sealed tubes. α-Ethylphenylhydrazine yields a monacetyl-derivative, which crystallises in needles and melts at 80°. The properties of α-isopropylphenylhydrazine, isobutyl-, isoamyl- and benzylphenylhydrazines, and their derivatives have already been described by the author (Abstr., 1887, 1104). *Acetylisopropylphenylhydrazine* crystallises in needles and melts at 101·5°. *Diphenylisopropylthiosemicarbazide* crystallises in colourless monoclinic plates $a : b : c = 1·2634 : 1 : 1·0487, \beta = 76° 32' 30''$. *Diisopropyldiphenyltetrazone* melts at 79°. No crystalline compounds of aldehydes or ketones with isopropylphenylhydrazine could be obtained. *Acetylisobutylphenylhydrazine* melts at 113—114°. *Diphenylisobutylthiosemicarbazide* melts at 140° and *diisobutyldiphenyltetrazone* at 106—107°. The *acetyl*-derivative of α-isoamylphenylhydrazine melts at 125°, the *thiosemicarbazide* at 160°, and *diisoamyldiphenyltetrazone* at 86·5°. The alcoholic solution of the tetrazone is decomposed by heat. *α-Benzylphenylhydrazine* melts at 26° and cannot be distilled without decomposition, even in a vacuum. With benzaldehyde, it forms a crystalline condensation product which melts at 111°. *Diphenylbenzylthiosemicarbazide* forms monoclinic crystals $a : b : c = 1·31075 : 1 : 1·68361, \beta = 62°·41' 5''$.

Benzyl chloride acts on α-benzylphenylhydrazine forming *dibenzyl phenylazonium chloride*, $NPh(C_7H_7)_2Cl·NH_2$; this crystallises in white needles and is freely soluble in water. It melts at 153—154°. The constitution of the condensation products of phenylhydrazine with aldehydes has been previously discussed (*loc. cit.*).

In the secondary unsymmetrical hydrazines the hydrogen in the amido-group cannot be displaced by sodium or potassium. When sodium acts on a secondary unsymmetrical hydrazine, a complicated reaction takes place resulting in the formation of a primary hydrazine.

W. C. W.

Action of Acid Chlorides and Anhydrides on Sodium Phenylhydrazine. By F. SCHMIDT (*Annalen*, **252**, 300—317).—Acetic anhydride reacts energetically with powdered sodium phenylhydrazine suspended in ether The crude product is washed with ether, and the residue repeatedly extracted with chloroform. On evaporating the chloroform, *β-acetylphenylhydrazine* crystallises in silky needles or plates. It melts at 128·5°. Acetic chloride acts on sodium phenylhydrazine suspended in ether, forming the preceding compound and *α-β-diacetylphenylhydrazine*, NPhAc·NHAc. The latter crystallises in colourless needles or plates, melts at 107—108°, and is freely soluble in alcohol, chloroform, and in hot water.

Acetylbenzylidenephenylhydrazone, NPhAc·N:CHPh, is prepared by heating benzylidenephenylhydrazone with twice its weight of acetic anhydride in sealed tubes at 190—200°. The product is poured into water and recrystallised from alcohol. The compound crystallises in needles, melts at 122°, and is freely soluble in chloroform. The hydrochloride of acetonephenylhydrazone is deposited in nacreous plates, when absolute ether is added to an alcoholic solution of acetonephenylhydrazone containing a small quantity of strong hydrochloric acid. The hydrochloride melts at 142°, is freely soluble in alcohol, and is decomposed by water. The *hydrobromide* melts at 132° with decomposition.

β-Butyrylphenylhydrazine, prepared by the action of butyryl chloride on sodium phenylhydrazine, melts at 113—114°. It is freely soluble in ether, alcohol, chloroform, and hot water. The isomeric α-compound appears to be formed at the same time in small quantities, but was not isolated. *Butyrylbenzylidenephenylhydrazone* is prepared by the action of normal butyric anhydride on benzylidenephenylhydrazone at 270°; it melts at 113·5° and is freely soluble in alcohol and ether.

In order to prepare α-benzoylphenylhydrazine, the sodium phenylhydrazine from 60 grams of phenylhydrazine and 8 grams of sodium is ground to powder under dry benzene, and brought into a 1½-litre flask; sufficient benzene is added to bring the volume of the liquid up to half a litre. The flask is surrounded by ice until the benzene begins to solidify; a mixture of 45 grams of benzoic chloride and 60 grams of benzene is then added in portions of 2 c.c. The flask is well cooled before each fresh addition of benzoic chloride. When the reaction is complete, the benzene is removed by distillation, and the residue is extracted with ether. α-Benzoylphenylhydrazine dissolves, but the greater portion of the β- and αβ-benzoylphenylhydrazine remains undissolved. In the course of some days the ethereal solution deposits crystals of β- and αβ-benzoylphenylhydrazines. The mother-liquor is saturated with carbonic anhydride to precipitate phenylhydrazine, the filtrate is evaporated to remove the ether, and the residue is poured into water and converted into sulphate. This salt crystallises in needles, and its solution is decomposed by sodium carbonate, yielding the free base. *α-Benzoylphenylhydrazine* melts at 70°, and is freely soluble in ether, alcohol, and chloroform. The hydrochloride and sulphate are sparingly soluble in water containing free acid; the hydrobromide and nitrate are freely soluble. The sparingly soluble sodium salt is decomposed by water. α-Benzoylphenylhydrazine unites with acetone, acetophenone, and benzaldehyde to form compounds melting respectively at 115·5°, 124°, and 122°. The *semicarbazide*, $N{\cdot}PhBzNH{\cdot}CO{\cdot}NH_2$, melts at 202° and the *thiosemicarbazide* at 310°. W. C. W.

Action of Phenylhydrazine on Tetrachloracetone. By S. Levy and F. C. Witte (*Annalen*, **252**, 343—349).—A compound of the composition, $C_{15}H_{12}N_4$ (probably $N\lessdot\genfrac{}{}{0pt}{}{NPh}{CH}>C<\genfrac{}{}{0pt}{}{NPh}{CH}\gtrdot N$), is formed when an alcoholic solution of symmetrical tetrachloracetone is boiled with phenylhydrazine. This substance crystallises in golden scales, and is freely soluble in the ordinary solvents. It melts at 126—127°, and boils above 300° with partial decomposition.

Fuming nitric acid converts it into a yellow, crystalline compound, $C_{15}H_{10}N_6O_5$. The new product is soluble in hot acetic acid and in warm chloroform, and melts at 234—235° with decomposition.

W. C. W.

Orthoparadinitrophenylphenylhydrazine, Dinitroso- and Nitronitroso-azobenzene. By C. Willgerodt and B. Hermann (*J. pr. Chem.* [2], **40**, 252—255).—The preparation of *orthoparadinitrophenylphenylhydrazine* (dinitrohydrazobenzene) has been already described (Abstr., 1888, 829); prolonged heating must be avoided.

Dinitrosoazobenzene (*loc. cit.*) may also be prepared by heating dinitrohydrazobenzene with alcohol in a reflux apparatus for 12 hours;

also by mixing a solution of phenylhydrazine hydrochloride in dilute alcohol with caustic alkali or alkaline carbonate, and adding an alcoholic solution of α-dinitrochlorobenzene. It melts at 178°, and at 140° sublimes in nearly white needles, which also melt at 178°.

Nitronitrosoazobenzene, $PhN_2\cdot C_6H_3(NO)\cdot NO_2$, obtained by heating α-dinitrohydrazobenzene with glacial acetic acid, crystallises in yellow needles melting at 175°; its sublimate melts at 160°. When heated with aqueous potash, it is converted into a phenol of higher melting point. A. G. B.

Unsymmetrical Secondary Aromatic Hydrazines containing Unsaturated Alcohol Radicles. By A. MICHAELIS and C. CLAESSEN (*Ber.*, **22**, 2233—2240).—*Unsymmetrical allylphenylhydrazine*, $NH_2\cdot NPh\cdot C_3H_5$, can be prepared by the reduction of allylphenylnitrosamine with zinc-dust and acetic acid, and together with about 5 per cent. of the symmetrical compound, by the action of allyl bromide on sodium phenylhydrazine, whilst it forms two-thirds of the product obtained by the action of allyl bromide on phenylhydrazine under the conditions employed by Fischer and Knoevenagel (Abstr., 1887, 932); the best yield is obtained by the second method. It is a colourless oil, and boils at 198° with slight decomposition under a pressure of 183·5 mm., at 183° under a pressure of 140 mm., and at 177° under a pressure of 109·5 mm. It reduces Fehling's solution on warming, and is readily soluble in dilute hydrochloric acid, yielding a solution which does not give the pyrazoline-reaction with aqueous potassium dichromate. When shaken in ethereal solution with yellow mercuric oxide, it is readily oxidised with the formation of a yellow, pungent compound which is volatile with steam, and yields an intense and persistent blue colour when its solution in dilute hydrochloric acid is treated with aqueous potassium dichromate. The *hydrochloride*, $NH_2\cdot NPh\cdot C_3H_5,HCl$, crystallises in white, silky, matted needles, melts at 137° and is readily soluble in water; the *benzoyl*-derivative, $NHBz\cdot NPh\cdot C_3H_5$ crystallises from alcohol in needles and melts at 139°; the *thiosemicarbazide*,

$$NHPh\cdot CS\cdot NH\cdot NPH\cdot C_3H_5,$$

crystallises from alcohol in very slender, matted needles and melts at 103°.

Benzylidenallylphenylhydrazone, $CHPh{:}N\cdot NPh\cdot C_3H_5$, crystallises in colourless needles, melts at 52° and is readily soluble in ether and hot alcohol.

Diallyldiphenyltetrazone, $C_3H_5\cdot NPh\cdot N{:}N\cdot NPh\cdot C_3H_5$, obtained by the action of dilute aqueous ferric chloride on allylphenylhydrazine, melts at 86° with decomposition and is readily soluble in ether and hot alcohol.

Unsymmetrical cinnamylphenylhydrazine, $NH_2\cdot NPh\cdot CH_2\cdot CH{:}CHPh$, is formed by the action of sodium phenylhydrazine on the product obtained by boiling cinnamic alcohol for half an hour with hydrobromic acid containing 47·8 per cent. of hydrogen bromide. It separates from ether in lustrous crystals, melts at 54°, is readily soluble in ether and alcohol, sparingly soluble in light petroleum, and in ethereal solution readily reduces yellow mercuric oxide with the formation of a feebly basic compound resembling that obtained from allylphenylhydrazine under like conditions. W. P. W.

Action of Phenylhydrazine on Phloroglucinol and Resorcinol. By A. BAEYER and E. KOCHENDOERFER (*Ber.*, **22**, 2189—2195).—When phloroglucinol is dissolved in a small quantity of absolute alcohol, treated with three molecular proportions of phenylhydrazine, and the mixture allowed to remain in the dark for 24 hours, crystalline aggregates of an additive compound, $C_6H_3(OH)_3,3NHPh{\cdot}NH_2$, separate and are purified by washing with cold benzene until the odour of phenylhydrazine can no longer be detected. This compound melts at 78—83°, is unstable, and decomposes into its constituents on treatment with alkali in the cold.

Disphenylhydrazophenol, $OH{\cdot}C_6H_3(NH{\cdot}NHPh)_2$ [$OH:(NH{\cdot}NHPh)_2 = 1:3:5$], is obtained when either the additive compound suspended in a small quantity of absolute alcohol or the mixture of phloroglucinol, phenylhydrazine, and alcohol employed in its preparation is allowed to remain for from four to six days in a well-closed vessel at the ordinary temperature; solution of the additive compound at first takes place, the liquid then becomes dark-orange or brown, and finally the hydrazophenol crystallises in prismatic forms. It crystallises from toluene in aggregates of colourless needles, melts at 143—144°, becomes only faintly yellow on exposure to the air, and is readily soluble in alcohol and ether. Alkalis dissolve it with a yellow, mineral acids with a reddish-yellow colour, and the solutions in the latter undergo complete decomposition on heating. Attempts to introduce a third phenylhydrazine residue into the molecule have not met with success. The *pentabenzoyl*-derivative, $C_{56}H_{38}O_6N_4$, is obtained by adding an excess of benzoic chloride to a solution of disphenylhydrazophenol in 10 per cent. aqueous soda. It crystallises from alcohol in well-formed white prisms, melts at 176°, is moderately soluble in alcohol, insoluble in water and dilute aqueous alkali, and is hydrolysed by prolonged boiling with concentrated aqueous soda.

Disphenylazophenol, $OH{\cdot}C_6H_3(N_2Ph)_2$ [$OH:(N_2Ph)_2 = 1:3:5$], is formed when disphenylhydrazophenol in alcoholic solution is oxidised by means of alcoholic ferric chloride. It crystallises from chloroform in beautiful, red, blunted needles, which show a steel blue colour by reflected light, melt at 176—177°, and dissolve readily in alcohol and ether, but less readily in chloroform. When heated with aqueous soda it dissolves, and the solution, on cooling, deposits golden scales of the *sodium*-derivative; this is decomposed on treatment with water. The *benzoyl*-derivative, $C_{25}H_{18}N_4O_2$, is obtained by the action of benzoic chloride on the sodium salt dissolved in dilute soda. It crystallises from chloroform in slender, feathery, red needles, sinters at 138°, melts at 148—150°, and is readily soluble in ethyl acetate, moderately soluble in alcohol and ether, and insoluble in dilute aqueous soda.

When resorcinol in alcoholic solution is treated with two molecular proportions of phenylhydrazine, an additive-compound, $C_6H_4(OH)_2 + 2PhNH{\cdot}NH_2$ is obtained, which crystallises in slender, white, satiny needles, melts at 76°, and is readily soluble in alcohol and ether. It decomposes with the formation of a brown, viscid mass on exposure to light and air, and is converted into its constituents when treated with aqueous soda or even water. Experiments undertaken with the object of preparing from this substance a condensation product analogous to that formed from the phloroglucinol additive-compound have not met with success. W. P. W.

Inorganic Derivatives of Phenylhydrazine. By A. Michaelis (*Ber.*, 22, 2228—2233).—*Thionylphenylhydrazone*, NHPh·N:SO, is prepared by adding thionyl chloride (42 grams) dissolved in twice its volume of ether to a carefully cooled solution of phenylhydrazine (100 grams) in ether (500 c.c.); a vigorous reaction takes place, and after removal of the ether by distillation, a pale yellow residue is obtained, which is repeatedly washed with water and finally crystallised from alcohol. It forms thick, sulphur-yellow prisms, melts at 105°, decomposes on distillation, but is readily volatile with steam and is easily soluble in ether, chloroform, carbon bisulphide, benzene, and hot alcohol. Dilute acids are practically without action on it, but on treatment with dilute alkali it decomposes readily and quantitatively into phenylhydrazine and the alkaline sulphite. When treated with bromine in ethereal solution, it is converted into diazobenzene perbromide, the sulphur appearing as sulphuric acid in the filtrate. On distillation, it yields a mixture of water, phenyl sulphide, and phenyl bisulphide, together with sulphurous anhydride and nitrogen.

Thionylethylphenylhydrazone, NEtPh·N:SO, is obtained when an ethereal solution of thionyl chloride is carefully added to a well-cooled solution of ethylphenylhydrazine in ten times its volume of ether. It is a reddish-yellow oil of peculiar aromatic odour, and closely resembles the preceding compound in its properties. It cannot be distilled without partial decomposition, but is volatile with steam. Dilute acids are practically without action on it, but it is readily decomposed by dilute alkali with the formation of ethylphenylhydrazine and the alkaline sulphite. W. P. W.

Some Reactions of Phenylhydrazine and of Hydroxylamine. By E. Fischer (*Ber.*, 22, 1930—1936).—*Oxalenediamidoxime*, $OH·N:C(NH_2)·C(NH_2):N·OH$, separates in colourless crystals when a rapid stream of cyanogen is passed into a concentrated, ice-cold aqueous solution of hydroxylamine hydrochloride (1 mol.) and potash (1 mol.), the whole being constantly shaken; the solution is filtered after a time and the filtrate treated again with cyanogen until in place of the crystals a colourless, amorphous compound is precipitated. The yield is about 40 per cent. of the hydroxylamine hydrochloride employed. Oxalenediamidoxime crystallises from hot water in thick, colourless prisms, melts at about 200° with decomposition, and is readily soluble in hot water but only moderately so in hot alcohol, and sparingly in ether, chloroform, and benzene. It dissolves in cold alkalis, but is reprecipitated by acetic acid; it is readily soluble in cold dilute hydrochloric acid, and from the hot concentrated acid the *hydrochloride* separates, on cooling, in long, colourless prisms. The *sulphate* crystallises from a warm dilute sulphuric acid solution of the base in long prisms. With Fehling's solution, aqueous solutions of the base give a characteristic reddish-brown precipitate of a copper compound; in very dilute solutions, a reddish-brown coloration is produced and precipitation occurs only on warming. It is completely decomposed when heated with 20 per cent. hydrochloric acid, yielding ammonia, hydroxylamine, and a small quantity of a compound which is rather sparingly soluble in cold water. It is readily soluble in hot acetic anhydride and, on cooling, the *diacetyl-derivative* separates in colourless crystals melting at 184° with decomposition.

A compound $C_6H_6N_4O_2$, probably an azoxime, is formed when the diacetyl-derivative (see above) is boiled for a long time with acetic anhydride; it crystallises from hot water in slender needles melting at 165—167°.

When oxalenediamidoxime is treated with excess of cyanogen, a colourless, amorphous precipitate is produced; this substance is insoluble in water, alcohol, and ether, is decomposed by boiling water, and is probably a mixture of oxalenediamidoxime and dicyanogen in molecular proportion.

Methenylphenylazidine, $NH\!:\!CH\!:\!N_2H_2Ph$ or $NH_2\cdot CH\!:\!N_2HPh$, is obtained, together with aniline and unchanged phenylhydrazine, when phenylhydrazine (10 grams) is heated at 100° for about two hours with hydrogen cyanide (2 c.c.) and water (5 grams). The yield is about 5 per cent. of the hydrazine employed. It crystallises from alcohol, melts at about 225° with decomposition, and is insoluble in water and only sparingly soluble in benzene and ether but readily in hot, dilute hydrochloric acid. The *hydrochloride* crystallises in yellowish needles. The *nitrate* crystallises in yellowish needles and is more readily soluble in hot water than the hydrochloride. The base reduces alcoholic ammoniacal silver nitrate solution and yields a flocculent nitrosamine which is insoluble in acids and gives Liebermann's reaction.

The compound $C_{14}H_{13}N_3O_3$ is formed when phenyl cyanate is shaken with a cold aqueous solution of hydroxylamine; it is insoluble in alkalis and does not reduce Fehling's solution, even on boiling.

The compound $NHPh\cdot CO\cdot NH\cdot OH$ is obtained when phenyl cyanate is added, drop by drop, to a large excess of hydroxylamine; it melts at 140°, is soluble in alkalis, and reduces Fehling's solution.

Phenylhydroxythiocarbamide, $NHPh\cdot CS\cdot NH\cdot OH$, is obtained when phenylthiocarbimide is shaken with a well-cooled aqueous solution of hydroxylamine in excess (compare Schiff, this Journal, 1876, ii 285). It is a colourless, crystalline compound, melts at 108° with decomposition, and dissolves unchanged in cold alkalis; on boiling the alkaline solution, it is completely decomposed and large quantities of phenylcyanamide are produced.

The compound $CO\!:\!S(N_2H_3Ph)_2$ separates in colourless crystals when carbonyl sulphide is passed into an ethereal solution of phenylhydrazine; it is decomposed at 100°, yielding hydrogen sulphide, ammonia, aniline, diphenylcarbamide, and diphenylcarbazide.

Diphenylcarbazide melts at 163—164°, that is 12° higher than stated by Skinner and Ruhemann (Trans., 1888, 551), and dissolves in alcoholic potash with a red coloration, being thereby converted into the compound $C_{13}H_{12}N_4O$, which crystallises in reddish-yellow needles melting at 157° with decomposition.

The compound NHPh·NH·COOEt is formed when phenylhydrazine (2 mols.) is treated with ethyl chlorocarbonate; it melts at 86—87°, distils with partial decomposition, and is converted into the corresponding azo-compound by mercuric oxide.

Carbonyl chloride reacts energetically with phenylhydrazine in ethereal solution, yielding diphenylcarbazide (m. p. 163—164°), phenylhydrazine hydrochloride, and a compound of higher melting point. F. S. K.

Action of Hydroxylamine on Thiocarbimides. By F. Tiemann (*Ber.*, **22**, 1939—1940; compare preceding abstract).—Hydroxylamine reacts with thiocarbimides in aqueous solution at the ordinary temperature, yielding monosubstituted hydroxythiocarbamides.

Phenylhydroxythiocarbamide, NHPh·CS·NH·OH, melts at 106°, (*loc. cit.*), the corresponding *orthotoluyl*-derivative, $C_6H_4Me·NH·CS·NH·OH$, at 92°, and α-naphthylhydroxythiocarbamide, $C_{10}H_7·NH·CS·NH·OH$, at 116°.

The hydroxythiocarbamides of the fatty series seem to be less stable.

Monosubstituted hydroxythiocarbamides are decomposed when heated, either in the dry state or in solution, yielding sulphur, water, and a monosubstituted cyanamide. *Orthotoluylcyanamide* melts at 77°, the corresponding *α-naphthyl*-derivative at 133°.

The substituted thiocarbamides obtained by treating α-alkylderivatives of hydroxylamine with thiocarbimides are much more stable, but when their aqueous solutions are boiled for a long time they are decomposed into sulphur, cyanamide, and the corresponding alcohol.

Phenylmethoxythiocarbamide, NHPh·CS·NH·OMe, melts at 116°, the corresponding *ethoxy*-derivative, NHPh·CS·NH·OEt, at 103°, and *phenylbenzoxythiocarbamide*, $NHPh·CS·NH·OC_7H_7$, at 115°.

Phenylbenzoxycarbamide, $NHPh·CO·NH·OC_7H_7$, is formed by the direct combination of phenyl cyanate (1 mol.) and α-benzylhydroxylamine; it is very stable and is only slowly decomposed by boiling hydrochloric acid, yielding α-benzylhydroxylamine hydrochloride. F. S. K.

Action of Chlorosulphonic Acid on Phenylthiocarbimide. By B. Pawlewski (*Ber.*, **22**, 2200—2202).—When warm phenylthiocarbimide is treated, drop by drop, with chlorosulphonic acid, a yellow compound is formed, hydrogen chloride being liberated in considerable quantity, together with a small proportion of sulphurous anhydride towards the end of the reaction. On extraction with boiling water, the yellow compound yields two substances, one soluble and the other insoluble in hot water.

The insoluble portion of the product has the composition $C_{14}H_{10}N_2S_3$, and is almost certainly identical with Proskauer and Sell's compound

$<\begin{matrix}S\cdot C(NPh)\\ S\cdot C(NPh)\end{matrix}>S$ (this Journal, 1877, i, 67). It crystallises in long, yellow, prismatic needles, melts at 149—151°, and is readily soluble in alcohol, ether, acetic acid, benzene, chloroform, aniline, &c.

The portion of the product soluble in water crystallises in large, colourless tables, which effloresce in the air and fall to powder. The crystals have the composition $SO_3H\cdot C_6H_4\cdot NCS + H_2O$; they do not melt, but lose water of crystallisation when heated. The compound is almost insoluble in alcohol and is sparingly soluble in boiling water.
W. P. W.

Ethylene Bases. By S. GABRIEL (*Ber.*, **22**, 2223—2227).—*β-Anilidoethylphthalimide*, $C_8H_4O_2{:}N\cdot CH_2\cdot CH_2\cdot NHPh$, is obtained when a mixture of bromethylphthalimide (20 grams) and aniline (15 grams) is introduced into an oil-bath heated at 150°; the temperature rapidly rises to 180°, and the reaction is complete at the end of 10 minutes. It crystallises from alcohol in lemon-yellow, pointed needles, melts at 99—100°, and has basic properties. It dissolves in aqueous alkalis on warming, and the solution on treatment with a quantity of acid equivalent to the alkali employed yields a viscid resinous precipitate which, on standing for a day, changes into a friable, crystalline solid. This compound in all probability consists of *anilidoethylphthalamic acid*, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot C_2H_4\cdot NHPh$, since it dissolves readily in acids and bases; it crystallises from alcohol as a powder, begins to sinter at 100°, melts at 120—130°, and is slowly converted into the phthalimide by boiling with water or alcohol.

Ethylenephenyldiamine, $NH_2\cdot CH_2\cdot CH_2\cdot NHPh$, is formed by boiling anilidoethylphthalimide with concentrated hydrochloric acid in a reflux apparatus for three hours, cooling, filtering off the separated phthalic acid, and evaporating to a syrup. The resulting hydrochloride, on decomposition with 33 per cent. aqueous potash, yields the base which boils at 262—264° (uncorr.), is miscible with water, forming a strongly alkaline solution, and withdraws carbonic anhydride from the air with the production of a crystalline carbonate. The *hydrochloride*, $C_8H_{12}N_2,HCl$, is neutral towards methyl-orange; the *hydrochloride*, $C_8H_{12}N_2,2HCl$, crystallises in light-green needles; the *hydrobromide*, $C_8H_{12}N_2,2HBr$, crystallises from alcohol in long, flat, colourless needles; the *picrate* crystallises from acetic acid in flat, yellow tables, and melts at 142—143°; the *platinochloride* forms sparingly soluble flat needles and tables.

In addition to β-anilidoethylphthalimide, a small quantity of the *diphthalyl*-derivative of diethylenephenyltriamine,

$$NPh(C_2H_4\cdot N{:}C_8H_4O_2)_2,$$

is also formed by the action of aniline on bromethylphthalimide. The best yield is obtained by heating a mixture of bromethylphthalimide (25 grams) and aniline (9 grams) for an hour at 100°, and then for a like period at 180°, dissolving the syrupy product in acetic acid (40 c.c.), and boiling with water (100 c.c.) for about five minutes; the insoluble brown precipitate is extracted with alcohol to remove any resinous matters, and the yellow residue crystallised from acetic acid.

It forms flat, sulphur-yellow needles, melts at 210—211°, is sparingly soluble in alcohol and has feeble basic properties. It dissolves in alcoholic potash on warming, and the solution on treatment with hydrochloric acid gives a resinous precipitate from which *anilidoethyldiphthalamic acid*, $NPh(C_2H_4{\cdot}NH{\cdot}C_6H_4{\cdot}COOH)_2$, can be separated.

Diethylenephenyltriamine, $NPh(CH_2{\cdot}CH_2{\cdot}NH_2)_2$, is obtained by boiling the diphthalyl-derivative (5 grams) with hydrobromic acid of sp. gr. = 1·49 (20 grams) for two hours in a reflux apparatus. It is an oil distilling at a temperature above 300°, is miscible with water, combines with carbonic anhydride forming a crystalline carbonate, and when heated at high temperatures with hydrobromic (or hydrochloric) acid is converted into a mixture of ethylenephenyldiamine and bromethylamine. The *hydrobromide*, $C_{10}H_{17}N_3,2HBr$, is a colourless, crystalline powder soluble in alcohol; the *picrate* crystallises from alcohol in long needles, begins to sinter at 190°, and melts at 200—202° with effervescence. W. P. W.

Selenium Compounds of the Benzene Series. By C. CHABRIÉ (*Compt. rend.*, **109**, 182—185).—Selenium tetrachloride reacts with benzene, and forms selenium subchloride, Se_2Cl_2, and mono-, di-, and trichlorobenzenes. It also acts on hydrocarbons of the methane and ethylene series, and with amylene, for example, yields amylene dichloride boiling at 143—148°.

In presence of aluminium chloride, selenium tetrachloride and benzene react with formation of crystalline selenophenol melting at 60°, phenyl selenide, and a red oil, which has the composition $Se_2Ph_3{\cdot}C_6H_4Cl$, and boils at 240—250° in a vacuum.

Selenophenol is insoluble in water, but dissolves in alcohol, and the solution gives a white precipitate with mercuric chloride; the fused substance is attacked by an aqueous solution of mercuric chloride.

Phenyl selenide $SePh_2$ (this vol., p. 41)), which is the chief product of the reaction, is an amber yellow liquid, boiling at 227—228° in a vacuum; sp. gr. at 20° = 1·450; vapour density by Meyer's method in an atmosphere of nitrogen at 360° = 8·17 (calc., 8·09). Phenyl selenide, unlike methyl selenide, does not combine with alkyl iodides, and in this respect it resembles phenyl sulphide. With bromine it yields *dibromophenyl selenide* $(C_6H_4Br)_2Se$, which crystallises from the alcohol in brilliant, white, hexagonal prisms, melting at 112°. When mixed with hydrogen peroxide and hydrochloric acid, and treated with a current of air, it yields a white, crystalline, hydroxychloride, $C_6H_4Cl{\cdot}Se{\cdot}C_6H_4{\cdot}OH$, which melts at 145°, dissolves in aqueous potash, and when treated with nitric acid yields a compound which crystallises in long needles melting at 188°.

Selenium, unlike oxygen and sulphur, has no action on benzene in presence of aluminium chloride. It reacts with zinc ethyl in the cold, yielding a white product, which is analogous to zinc mercaptan, and is decomposed by dilute hydrochloric acid, with liberation of a compound having a fœtid odour similar to that of Wöhler's ethyl hydroselenide.

Selenium, even when heated, has no action on mercury phenyl dissolved in benzene, nor on aluminium phenyl dissolved in xylene.

C. H. B.

Action of Phosphonium Iodide on Benzaldehyde. By S. LITTHAUER (*Ber.*, **22**, 2144—2148).—When phosphonium iodide (10 grams) is digested with benzaldehyde (5 grams) at 100° for 4 to 5 hours, a mixture of hydrogen phosphide and hydrogen iodide escapes on opening the tube, and a product is obtained consisting of three substances, one of which is soluble in water. A better yield is obtained when the proportion of benzaldehyde is raised to 13 grams, and under these conditions hydrogen phosphide is absent from the gas evolved on opening the tube.

Benzylphosphinic acid, $C_7H_7 \cdot PO(OH)_2$, forms the soluble constituent of the product. It crystallises from acetic acid in stellate groups of prisms, melts at 166°, and is soluble in alcohol, but insoluble in benzene, chloroform, ether, and light petroleum. It liberates carbonic anhydride from carbonates. The crystalline *silver* salt, $C_7H_7 \cdot PO_3Ag_2$, was prepared.

Nitrobenzylphosphinic acid, $NO_2 \cdot C_7H_6 \cdot PO(OH)_2$, obtained by the action of fuming nitric acid in the cold, crystallises in yellow needles, decomposes without previous fusion at 217°, and is sparingly soluble in ether, soluble in alcohol and much water.

Dibenzylphosphinic acid, $P(C_7H_7)_2O \cdot OH$, can be separated from the product insoluble in water by extraction with aqueous potash, and subsequent precipitation with an acid. It crystallises in large, silvery scales, melts at 191°, and is insoluble in water, very sparingly soluble in ether, chloroform, benzene, and light petroleum, and soluble in alcohol. It neither reddens blue litmus-paper, nor liberates carbonic anhydride from carbonates. The *potassium* salt, $PC_{14}H_{14}O_2K$, and *silver* salt, $PC_{14}H_{14}O_2Ag$, are described; the *methyl* salt, $P(C_7H_7)_2O \cdot OMe$, crystallises in tufts of silky prisms, melts at 75°, and is soluble in alcohol and light petroleum.

Dinitrodibenzylphosphinic acid, $P(C_7H_6 \cdot NO_2)_2O \cdot OH$, obtained by the action of fuming nitric acid in the cold, crystallises in yellow cubes, melts at 210—212°, and is soluble in acetic acid.

The third constituent of the product, insoluble both in water and in alkali, is tribenzylphosphine oxide. W. P. W.

Mononitrated Hydroxybenzaldehydes and their Methyl Ethers. By F. TIEMANN (*Ber.*, **22**, 2339—2346).—The author gives a *résumé* of the work done on this group of compounds, and shows that of the ten possible isomerides of each group, five are known in the hydroxy-, and six in the methoxy-group.

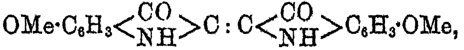
The following table shows our present knowledge of the constitution of these compounds :—

OH or COH : NO_2 : OMe.	Nitro-hydroxy-benzaldehydes. m. p.	Nitromethoxybenz-aldehydes. m. p.
1 : 3 : 2	110°	—
1 : 4 : 2	—	—
1 : 5 : 2	126°	89°
1 : 6 : 2	—	—
1 : 2 : 3	—	102°
1 : 4 : 3	—	63°
1 : 5 : 3	128°	104°
1 : 6 : 3	166°	83°
1 : 2 : 4	—	—
1 : 3 : 4	142°	83·5°

L. T. T.

The Four Isomeric Nitrometamethoxybenzaldehydes. By F. Rieche (*Ber.*, **22**, 2347—2364).—The author has carefully examined the three nitrometamethoxybenzaldehydes obtained by the action of nitric acid on metamethoxybenzaldehyde. The product of nitration is dissolved in boiling benzene, and from this solution orthonitrometamethoxybenzaldehyde, [COH : NO_2 : OMe = 1 : 2 : 3] (m. p. 102°), crystallises out on cooling. The benzene is evaporated from the mother-liquor, and the residue distilled in steam, when orthonitrometamethoxybenzaldehyde, [COH : OMe : NO_2 = 1 : 3 : 6] (m. p. 83°), passes over, and metanitrometamethoxybenzaldehyde, [COH : OMe : NO_2 = 1 : 3 : 5] (m. p. 104°), remains behind, and may be crystallised from alcohol.

The 1 : 2 : 3 compound is easily soluble in alcohol, ether, boiling benzene, chloroform, glacial acetic acid, and acetone, forms an easily soluble hydrogen sodium sulphite derivative, and gives the indigo reaction with acetone and soda. Its *oxime* is easily soluble in alcohol, ether, benzene, chloroform, and alkali, sparingly in boiling water, and melts at 170°. The aldehyde is re-formed when the oxime is dissolved in caustic soda and sodium nitrite, and then sulphuric acid added. The *phenylhydrazone* forms orange needles melting at 134°, and easily soluble in alcohol, ether, and chloroform.

Dimethoxyindigo,  $\mathrm{OMe{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C:C{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C_6H_3{\cdot}OMe}$, is formed when a few drops of caustic soda are added to the acetone solution of the aldehyde. It crystallises from chloroform in glistening blue needles, which fluoresce violet in reflected light. It sublimes in thin violet scales. When treated in alkaline solution with potassium permanganate or silver oxide, the aldehyde is oxidised to *orthonitrometamethoxybenzoic acid*, COOH : NO_2 : OMe = 1 : 2 : 3, which is soluble in alcohol, acetone, and boiling water, crystallises in white scales, and melts at 251°. When digested with ammonia, the methoxy-group is displaced by NH_2, and this by the action of potash is again displaced by hydroxyl. The hydroxy-acid thus formed is identical with that examined and proved to be the 1 : 2 : 3 acid by Griess (Abstr., 1879, 246).

The 1 : 3 : 6 aldehyde forms an easily soluble compound with sodium hydrogen sulphite. The *oxime* is soluble in alcohol, ether, and chloroform, and melts at 152°; the *phenylhydrazone* forms blood-red prisms melting at 154°, and soluble in alcohol, benzene, and chloroform. Oxidation of the aldehyde in alkaline solution yields the corresponding *methoxy-acid* melting at 132—133°.

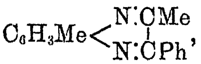
The 1 : 3 : 5 aldehyde does not give the indigo reaction, and is scarcely volatile in steam. The *oxime* is more soluble than those of the orthoaldehydes, and melts at 148°. The hydrazone crystallises in red scales melting at 126°. On oxidation in either acid or alkaline solutions, the aldehyde yields *metanitrometahydroxybenzoic acid*, which crystallises in white needles, begins to sublime at 225°, and melts at 233°.

Paranitrometamethoxybenzaldehyde (1 : 3 : 4) was prepared both by Ulrich's (Abstr., 1886, 60) and Landsberg's (Abstr., 1887, 483) methods. It is volatile in steam, and melts at 63°. The *oxime* forms crystals melting at 93°; the *phenylhydrazone* flesh-coloured needles melting at 103°. The corresponding benzoic acid is sparingly soluble in boiling water, easily in alcohol, chloroform, and glacial acetic acid, and melts at 208°. L. T. T.

Mixed α-Diketones. By H. MÜLLER and H. v. PECHMANN (*Ber.*, **22**, 2127—2133; compare Otte and v. Pechmann, p. 1137).—α-Diketones in which the radicle —CO·CO— is united, on the one hand with an aromatic, and on the other with a non-aromatic radicle are termed by the authors "mixed" α-diketones. Such compounds can be prepared by decomposing the corresponding oxime by boiling with dilute sulphuric acid, as already described in the case of diacetyl (Abstr., 1888, 811), but the yield is less satisfactory than in the case of the non-aromatic α-diketones. The mixed diketones are yellow, oily liquids, which are volatile without decomposition, do not solidify, and have a slightly sweet but at the same time powerful odour. Unlike the non-aromatic compounds, they are heavier than, and are practically insoluble in water, but in their reactions with alkalis, diazobenzenesulphonic acid, phenylhydrazine, &c., they closely resemble the non-aromatic α-diketones. Under certain conditions, they decompose into an aldehyde and an acid, and in the case of methyl phenyl diketone, when treated with potassium cyanide and alcohol by Jourdan's method (Abstr., 1883, 805), the products obtained are benzaldehyde and acetic acid.

Acetylbenzoyl (ω-phenyl-αω-diketopropane), COMe·COPh, is obtained from α-nitrosopropiophenone (Abstr., 1888, 1087) by boiling with 30 to 35 times its weight of 5 per cent. sulphuric acid. It boils at 164—165° under a pressure of 116 mm., and at 216—218° under the ordinary pressure, has a sp. gr. = 1·1041 at 14° (compared with water at 4°), and dissolves in about 380 parts of water at 20° forming a pale-yellow solution. The *hydrazone*, $C_{15}H_{14}N_2O$, crystallises in small, yellow needles, melts at 143—145°, and is readily soluble in alcohol, benzene, and chloroform; the *osazone*, $C_{21}H_{20}N_4$, forms yellow, granular crystals, melts at 104—105°, and is soluble in ether, benzene, alcohol, and chloroform; the *ωα-hydrazoxime*,

$$OH{\cdot}N{:}CMe{\cdot}CPh{:}N{\cdot}NHPh,$$

obtained by the action of phenylhydrazine on α-nitrosopropiophenone, crystallises from benzene in white needles, and melts at 202°; the *dioxime*, $OH{\cdot}N{:}CMe{\cdot}CPh{:}N{\cdot}OH$, crystallises from dilute alcohol in colourless needles, melts at 235—236°, and is soluble in alcohol and ether, insoluble in water, chloroform, and benzene. Acetylbenzoyl and toluylenediamine dissolved in ether in molecular proportion yield *methylphenltoluquinoxaline*,  $C_6H_3Me<\begin{array}{l}N{:}CMe\\ \quad\vert\\ N{:}CPh\end{array}$, which crystallises with difficulty, melts at 46—48°, and is readily soluble in the ordinary solvents, but insoluble in water. When the diketone is treated with 20 parts of water and 2 parts of 10 per cent. aqueous potash together with a small quantity of potassium ferricyanide, and the mixture allowed to remain for 12 hours, then heated on a water-bath for 15 minutes, and afterwards extracted with hot benzene, a substance is obtained (after the evaporation of the benzene), which, when warmed with 6 parts of alcohol and 3 parts of dilute nitric acid until the colour has become pure yellow, is converted into *paradiphenylquinone*, $C_6H_2O_2Ph_2$. This crystallises from acetic acid in orange-yellow scales, melts at 214°, dissolves in concentrated sulphuric acid with a reddish-violet colour, and is sparingly soluble in most solvents. On reduction with zinc-dust and acetic acid, it yields the corresponding *quinol;* this crystallises from dilute alcohol in colourless cubes, melts at 218—219°, and on oxidation with ferric chloride forms first a dark-green quinhydrone, and finally paradiphenylquinone.

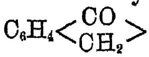
Propionylbenzoyl (ω-phenyl-$\alpha\omega$-diketobutane) $COEt{\cdot}COPh$, is obtained by the hydrolysis of nitrosobutyrophenone. It is a viscid, yellow oil, which boils at 238—240°, has a powerful odour, is readily volatile with steam, and is almost insoluble in water. Although stable when pure and preserved in well-closed vessels, it decomposes when moist, particularly in ethereal solution, with the formation of benzoic acid and an aldehyde, probably propaldehyde.

Phenyldiacetyl (ω-phenyl-α-β-diketobutane), $COMe{\cdot}CO{\cdot}CH_2Ph$, is prepared by boiling nitrosobenzylacetone with 30 to 40 parts of 10 per cent. hydrochloric acid, and $\frac{1}{4}$ part of ferric chloride for 30 minutes in a reflux apparatus, and steam-distilling the product. It is a thick, yellow oil of honey-like odour, boils at 175—176°, and has a sp. gr. = 1·0721 at 14° (compared with water at 4°). The *osazone*, $C_{22}H_{22}N_4$, crystallises from alcohol in colourless, silky, flat needles, and melts at 172—173°. W. P. W.

Orthotolyl-β-imidobutyric Acid. By B. PAWLEWSKI (*Ber.*, 22, 2203).—Orthotolyl-β-imidobutyric acid (compare Knorr, Abstr., 1884, 1198), $C_6H_4Me{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOH$, crystallises in long, prismatic needles, melts at 110—112°, resolidifies at 85—87°, has a sp. gr. = 1·242 at 20° (compared with water at 20°), and is soluble in alcohol and hot water, but almost insoluble in cold water. W. P. W.

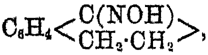
Action of Orthocyanobenzyl Chloride on Ethyl Sodacetoacetate. By S. GABRIEL and J. HAUSMANN (*Ber.*, **22**, 2017—2019).—*Ethyl orthocyanobenzylacetate*, $CN\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COOEt$, is obtained, together with very small quantities of ethyl diorthocyanobenzylacetoacetate, when ethyl sodacetoacetate is warmed with orthocyanobenzyl chloride in alcoholic solution. It crystallises from hot methyl alcohol in colourless needles and plates, melts at 98—99°, and is readily soluble in most ordinary solvents. It dissolves unchanged in cold concentrated hydrochloric acid, but when the solution is kept for some time, or warmed, it is decomposed into α-hydrindone, carbonic anhydride, alcohol, and ammonia.

Ethyl diorthocyanobenzylacetoacetate, $CAc(CH_2\cdot C_6H_4\cdot CN)_2\cdot COOH$, crystallises from alcohol in colourless prisms, melts at 120°, and is readily soluble in the ordinary solvents.

α-Hydrindone,  $C_6H_4<\begin{matrix}CO\\CH_2\end{matrix}>CH_2$, crystallises in rhombic plates, melts at 40°, boils at 243—245°, and is very readily soluble in all the ordinary solvents. It has a peculiar odour and a bitter taste; it dissolves unchanged in cold concentrated hydrochloric acid and with hydriodic acid (b. p. 127°) it yields a crystalline compound which is decomposed by water. (Compare next abstract.)

F. S. K.

Action of Orthocyanobenzyl Chloride on Ethyl Sodomalonate. α-Hydrindone. By J. HAUSMANN (*Ber.*, **22**, 2019—2026).—*Ethyl disorthocyanobenzylmalonate*, $C(CH_2\cdot C_6H_4\cdot CN)_2(COOEt)_2$, is formed together with ethyl cyanobenzylacetate (m. p., 98°; see preceding abstract) when orthocyanobenzyl chloride is warmed with ethyl malonate in alcoholic solution; the two compounds can be separated by extracting the crude product with cold hydrochloric acid. It crystallises from alcohol in prisms, melts at 86°, and is readily soluble in the ordinary solvents.

α-Hydrindoneoxime,  $C_6H_4<\begin{matrix}C(NOH)\\CH_2\cdot CH_2\end{matrix}>$, crystallises from alcohol in colourless needles, melts at 146°, and is soluble in alkalis. The *hydrazone*, $C_{15}H_{14}N_2$, crystallises from alcohol in colourless prisms, turns brown at 120°, and melts at a somewhat higher temperature; it dissolves freely when boiled with most of the usual solvents, and it gradually decomposes on exposure to the air.

A compound, $C_{15}H_{11}N$, probably orthobenzyleneindole, is formed when hydrindonehydrazone is boiled for a few minutes with concentrated hydrochloric acid. It crystallises from alcohol in colourless, rhombic plates, and from benzene in needles; it softens and is partially decomposed at about 235°, and it is only sparingly soluble in boiling ether, alcohol, or benzene.

A compound, $(C_9H_6)_n$, probably triorthobenzylenebenzene, is obtained when hydrindone is heated at 100° for three or four hours with concentrated hydrochloric acid. It crystallises from boiling cumene or nitrobenzene in small, yellowish needles, does not melt below 280°, and is almost insoluble in most ordinary solvents. When treated with chromic acid in boiling glacial acetic acid solution, it yields a compound which crystallises in slender, lemon-yellow needles. The same compound, $(C_9H_6)_n$, is obtained, together with small quantities of an oil, when hydrindone is heated at 230° with hydriodic acid and amorphous phosphorus, or when it is distilled over zinc-dust.

Dichlorindene, $C_9H_6Cl_2$, is formed when hydrindone (2 grams) is heated with phosphoric chloride (6·4 grams); it crystallises from methyl alcohol in colourless prisms, melts at 29°, and dissolves freely when boiled with most of the ordinary solvents.

Dibromhydrindone, $C_9H_6Br_2O$, prepared by treating hydrindone (1·3 grams) with bromine (3·2 grams) in chloroform solution, crystallises from alcohol in colourless prisms, melts at 133—134°, and dissolves freely in most ordinary solvents when warmed therewith.

F. S. K.

Derivatives of Parahydroxyphenylacetic Acid. The Ethereal Oil of White Mustard. By H. SALKOWSKI (*Ber.*, **22**, 2137—2144). —Parahydroxybenzyl cyanide, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, is best prepared by gradually adding the calculated quantity of sodium nitrite in aqueous solution to a boiling and strongly acid solution of paramidobenzyl cyanide; the yield amounts to 85 per cent. of that theoretically possible. It forms triclinic crystals, agreeing in their crystallographic characters with those of the nitrile obtained by Will and Laubenheimer from the sinalbin present in white mustard seed (Abstr., 1880, 265), melts at 69—70°, and boils at 330·5° (thermometer in vapour) under a pressure of 756·5 mm. On methylation, it yields *paramethoxybenzyl cyanide*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, which boils at 286—287° (thermometer in vapour) under a pressure of 761 mm., has a sp. gr. = 1·10013 at 0°, 1·09346 at 8·5°, 1·08685 at 16·8°, 1·08485 at 19·5°, and 1·08454 at 20° (compared with water at 4°), and gives a coefficient of refraction $n_D = 1·53175$ at 16·8°, and a dispersion $n_F - n_D = 0·0118862$.

Parahydroxyphenylacetamide, obtained by heating ethyl parahydroxyphenylacetate with aqueous ammonia, crystallises in large, colourless scales, and melts at 175°. *Paramethoxyphenylacetamide*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared by the hydrolysis of the cyanide with strong sulphuric acid, crystallises from alcohol in lustrous scales, melts at 188—189°, and is sparingly soluble in cold alcohol, insoluble in water.

Methyl parahydroxyphenylacetate is an oily liquid with a peculiar, slight, persistent odour; it boils at 310° (thermometer in vapour) under a pressure of 760·5 mm., has a sp. gr. = 1·19477 at 0°, 1·18668 at 10°, and 1·17863 at 20° (compared with water at 4°), and gives a coefficient of refraction $n_D = 1·5338$ at 18·5°, and a dispersion $n_F - n_D = 0\ 0117132$. The *ethyl* salt boils at 314° (thermometer in vapour) under a pressure of 760·5 mm., has a sp. gr. = 1·13856 at 0°, 1·13047 at 9·5°, and 1·12255 at 18 5° (compared with water at 4°), and gives a coefficient of refraction $n_D = 1·5183$ at 20°, and a dispersion $n_F - n_D = 0·01071$.

Parahydroxybenzylamine, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2 + H_2O$, can be prepared by heating paramethoxyphenylacetamide with bromine and alkali by Hofmann's method, and subsequently eliminating the methyl-group by heating the product either with hydriodic or strong hydrochloric acid at 130°. The yield is poor, the chief product obtained by the action of bromine and alkali on the cyanide being *bromoparamethoxyphenylacetic acid*. $OMe\cdot C_6H_3Br\cdot CH_2\cdot COOH$, which crystallises in colourless scales, melts at 114—115°, and is almost insoluble in water, readily soluble in alcohol. A second method of preparation consists in treating a hot and strongly acid solution of paramidobenzylamine (Amsel and Hofmann, Abstr., 1886, 698) with the calculated quantity of sodium nitrite. Parahydroxybenzylamine crystallises in lustrous, rhombic tables, and melts at 95° with effervescence. The *hydrochloride*, C_7H_9NO,HCl, crystallises in large, lustrous tables, and is readily soluble in water and alcohol, and the *platinochloride*, $(C_7H_9NO)_2,H_2PtCl_6 + 2H_2O$, crystallises in stellate groups of flat needles.

Parahydroxybenzylthiocarbimide, $OH\cdot C_6H_4\cdot CH_2\cdot NCS$, is obtained by adding carbon bisulphide to an alcoholic solution of parahydroxybenzylamine and subsequently treating it with a solution of mercuric chloride. It has all the properties of, and is identical with, white mustard oil, has a burning taste, dissolves in dilute alkalis, and is insoluble in water.

Paramidobenzylamine can be prepared by Gabriel's method (Abstr., 1887, 1037) from paranitrobenzyl chloride by gently heating it with potassium phthalimide. The resulting *paranitrobenzylphthalimide* crystallises from acetic acid in yellow prisms, melts at 174—175°, and when heated at 190° with fuming hydrochloric acid is converted into paramidobenzylamine and phthalic acid. In addition to the platinochloride, $(C_7H_{10}N_2,2HCl)_2PtCl_4$, described by Amsel and Hofmann (*Ber.*, **19**, 1288), paramidobenzylamine yields a second salt,

$$C_7H_{10}N_2,H_2PtCl_6 + H_2O,$$

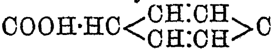
crystallising in golden-yellow needles. W. P. W.

Pyranilpyroic Acid and Mesaconilic Acid. By A. REISSERT (*Ber.*, **22**, 2281—2298).—In reply to the criticisms of Anschütz (Abstr., 1888, 1092) and Anschütz and Hensel (this vol., p. 258), the author points out that in his previous work (Abstr., 1888, 694) he has regarded pyranilpyrolactone and Gottlieb's citraconanil as identical (compare Michael, *Amer. Chem. J.*, **9**, 180), and employed the former in the preparation of the oxidation-product and the latter in that of the reduction-products there described, whereas later investigation shows that the two compounds are distinct. It follows, therefore, that the so-called reduction-products of pyranilpyrolactone are in reality those of citraconanil, as Anschütz has pointed out (*loc. cit.*). The opinion expressed by Anschütz, that pyranilpyroic acid is actually mesaconilic acid (Abstr., 1888, 1092) is, however, erroneous, and there can be little doubt that in his investigations he employed the acid obtained by the condensation of aniline with citraconic acid or anhydride. A comparison of the properties of these substances shows that, whereas pyranilpyroic acid decomposes partially on drying at 100°, dissolves very sparingly in dilute alcohol, crystallises in small and slightly coloured needles, melts at 165°, and forms an indistinctly crystalline silver salt; mesaconilic acid is stable at 100°, separates from ether alcohol in white crystals which in the moist state readily become bright-red, melts at 175°, and forms an uncrystallisable silver salt. Moreover, pyranilpyrolactone crystallises from dilute alcohol in colourless, slender, matted needles, melts at 96°, and is extremely soluble in alcohol, sparingly soluble in water, whilst citraconanil crystallises from dilute alcohol in pale-yellow, long, brittle needles, melts at 98°, and is readily soluble in strong alcohol, but practically insoluble in water. The difference between the two substances is further illustrated by a comparison of the products obtained from each by oxidation and reduction.

A repetition of the oxidation of pyranilpyroic acid with potassium permanganate leads to results similar for the most part to those previously described. The oxidation-products consist of oxanilic acid, which crystallises in lustrous scales or silky needles melting at 149—150°, and anilosuccinic acid, which forms yellowish, lustreless, crystals melting at 151—152°. The lustrous crystals of anilosuccinic acid previously described must therefore have contained some oxanilic acid. When heated at 100°, anilosuccinic acid is converted, as stated, into β-anilopropionic acid with the elimination of the theoretical quantity of carbonic anhydride; the acid so obtained melts at 153°, and corresponds in its properties with the acid previously described. Mesaconilic acid, on the contrary, requires less potassium permanganate by one-third for its oxidation, and yields oxanilic acid as sole product.

On reduction with zinc-dust in acetic acid solution, pyranilpyroic acid decomposes with the formation of carbonic anhydride, aniline, and a small quantity of a liquid acid consisting probably of either butyric or isobutyric acid. Mesaconilic acid, on the other hand, is reduced in the way described by Anschütz, and the author admits that the substances termed by him dihydropyranilpyrolactone, deoxypyranilpyroic acid, and bromodeoxypyranilpyroic acid, are pyrotartaric-anilide, pyrotortaric-anilic acid, and pyrotartaric-parabromanilic acid respectively. When pyrotartaric-anilic acid is brominated at the ordinary temperature with an aqueous solution of bromine, no tribromanilide, contrary to the statement of Anschütz and Hensel, is formed, and the pyrotartaric-parabromanilic acid obtained melts at 165° and not at 158—158·5°.

The condensation compound obtained from citraconanil and phenylhydrazine has been already described (Abstr., 1888, 695). With pyranilpyrolactone, phenylhydrazine yields a compound, $C_{17}H_{17}N_3O_2$, which crystallises in small, white needles, melts at 158—159°, and agrees in its properties with the so-called phenylhydrazide of citraconanil. When boiled with aqueous potash, this compound, prepared by either method, is converted into a substance which crystallises from dilute alcohol or water in needles, melts at 183°, and is insoluble in alkalis and acids. The constitution of this compound, and of the substances formed by the action of phenylhydrazine on lactones, will form the subject of a later communication. W. P. W.

Constitution of Benzene. Reduction-products of Terephthalic Acid. By A. v. BAEYER. Part II (*Annalen*, **251**, 257—311).—In the first part of this research (Abstr., 1888, 1069) the author has demonstrated that all the reduction-products of terephthalic acid exhibit the character of saturated or unsaturated fatty acids. They do not resemble benzene-derivatives. The unsaturated hydroterephthalic acids contain single and double linkings. All the 10 hydro-acids which are theoretically possible have been prepared.* The $\Delta^{1\cdot4}$ dihydroterepthalic acid, previously described (Abstr., 1888, 1072) as the primary product of the reduction of terephthalic acid by sodium amalgam, is really the result of a secondary reaction, namely the action of sodium hydroxide on $\Delta^{2:5}$ dihydroterephthalic acid. If the free alkali is neutralised by carbonic anhydride, during the operation of reducing the terephthalic acid, the $\Delta^{2:5}$ dihydro-acid can be isolated. The constitution of the $\Delta^{2:5}$ acid,  $COOH{\cdot}HC{<}{\genfrac{}{}{0pt}{}{CH{:}CH}{CH{:}CH}}{>}CH{\cdot}COOH$, is based on the following facts. The acid is not attacked by sodium amalgam at the ordinary temperature. It unites directly with four atoms of bromine. Two of the hydrogen-atoms are loosely attached

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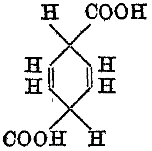
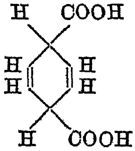
* The author gives the following scheme for the constitutions and nomenclature of the 10 possible hydroterephthalic acids :—

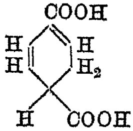
Dihydroterephthalic acids, $C_6H_6(COOH)_2$.



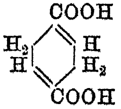
$\Delta^{2,5}$ or $\lceil^{\text{cistrans}}\Delta^{2,5}$.



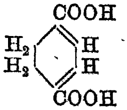
$\lceil^{\text{cis}}\Delta^{2,5}$.



$\Delta^{1,5}$.

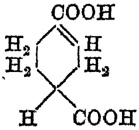


$\Delta^{1,4}$.

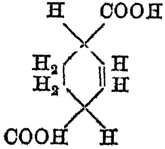


$\Delta^{1,3}$.

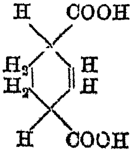
Tetrahydroterephthalic acids, $C_6H_8(COOH)_2$.



Δ^{1}.

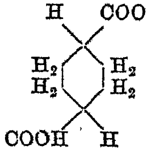


Δ^{2} or $\lceil^{\text{cistrans}}\Delta^{2}$.

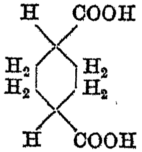


$\lceil^{\text{cis}}\Delta^{2}$.

Hexahydroterephthalic acids, $C_6H_{10}(COOH)_2$.



$\lceil^{\text{cistrans}}$.



$\lceil^{\text{cis}}$.

to the rest of the molecule. It is transformed into the $\Delta^{1:5}$ dihydro-acid by boiling with water, and into the $\Delta^{1:4}$ acid by a boiling solution of sodium hydroxide.

The $\Delta^{2:5}$ dihydro-acid exists in two modifications differing in solubility and in melting point; these different modifications are geometrical isomerides.

Γ^{cistrans} $\Delta^{2:5}$ *Dihydroterephthalic acid* is deposited from its solution in ethyl acetate in monoclinic prisms, $a : b : c = 0{\cdot}98203 : 1 : 1{\cdot}0188$, $\beta = 78° 2'$. It is moderately soluble in ether, but it requires 310 parts of cold water for complete solution. The barium salt crystallises in plates and is freely soluble in water; the microscopic prismatic crystals of the cadmium salt are less soluble. The silver salt forms quadratic prisms. A warm solution of the acid readily reduces silver nitrate. This reaction and the oxidation of the acid to terephthalic acid by an alkaline solution of potassium permanganate distinguish this compound from all other reduction-products of terephthalic acid. The methyl salt melts at 77° and unites with bromine, yielding a dibromide and a tetrabromide. Exposure to a temperature of 100° for six hours converts the methyl salt into methyl terephthalate.

Γ^{cis} $\Delta^{2:5}$ *Dihydroterephthalic acid* is extracted from the mother-liquor from which the cistrans-isomeride has been deposited, by agitating it with ether. The two geometrical isomerides closely resemble each other in their chemical properties, but the cis-acid and its salts are distinguished from the corresponding cistrans compounds by the greater solubility of the former.

The $\Delta^{1:5}$ dihydroterephthalic acid is formed when the $\Delta^{2\cdot5}$ dihydro-acid is boiled in water, and it is converted into the $\Delta^{1:4}$ acid by the action of sodium hydroxide. Sodium amalgam at the ordinary temperature reduces the $\Delta^{1\cdot5}$ dihydro-acid to Δ^{2} tetrahydroterephthalic acid. Any changes which increase the acid character of the carboxyl-group in a non-saturated compound also facilitate the reduction of the double linkings in the compound. The existence of the unstable β-γ-double linking in the methyl salt of the $\Delta^{1:5}$ dihydroterephthalic acid accounts for the fact that this crystalline substance spontaneously changes into a resinous mass.

$\Delta^{1:4}$ dihydroterephthalic acid has been previously described (*loc. cit.*). It unites with hydrobromic acid yielding paradibromohexahydroterephthalic acid. When $\Delta^{1:4}$ dihydroterephthalic acid is treated with sodium amalgam at the ordinary temperature the greater part of the acid remains unchanged, but a small quantity of the two geometrical isomeric tetrahydroterephthalic acids (Δ^{2}) is formed.

Alcoholic potassium hydroxide converts *aa'* dibromohexahydroterephthalic acid (Abstr. 1888, 1074) and the dibromide of the Δ^{2} tetrahydro-acid into $\Delta^{1:3}$ dihydroterephthalic acid. This compound unites with hydrobromic acid to form a dibromhexahydro-acid, which contains the bromine atoms in the ortho-position. Under similar conditions the $\Delta^{1:4}$ dihydro-acid yields a para-compound. The $\Delta^{1:3}$ dihydro-acid is easily reduced by sodium amalgam, or by zinc-dust and acetic acid, forming both the geometrical isomeric forms of Δ^{2} tetrahydroterephthalic acid. It appears probable that both the double linkings are simultaneously attacked, and a hydrogen-atom attaches itself to each of the carbon atoms united to a carboxyl-group, and a new double linking is formed between the two β-carbon-atoms. An analogous change occurs on the reduction of dichloromuconic acid to hydromuconic acid. The $\Delta^{1:3}$ dihydro-acid is transformed into the $\Delta^{1:4}$ acid by the action of a boiling solution of sodium hydroxide. The barium salt of the $\Delta^{1:3}$ acid is soluble in hot water, and is deposited from the solution in glistening needles, on cooling. The acid is rapidly oxidised by an alkaline solution of potassium permanganate. The methyl salt is soluble in ether and in light petroleum. It crystallises in monoclinic plates, $a : b : c = 2{\cdot}2408 : 1 : 3{\cdot}5907$, $\beta = 87° 13'$. Hydrobromic acid slowly attacks the methyl salt and forms 2 : 3 dibromhexahydroterephthalic acid. On reduction with zinc-dust and acetic acid, the dibromo-derivative yields Δ^2 tetrahydroterephthalic acid. This acid can also be prepared by the reduction of the $\Delta^{1:3}$ or $\Delta^{1:5}$ dihydro-acid. Γ^{cistrans} Δ^2 *Tetrahydroterephthalic acid* melts at about 220°, and is much more soluble in water than the isomeric Δ^1 acid. The barium and cadmium salts are also more soluble than the corresponding salts of the isomeric acid. The methyl salt is crystalline. It melts a little above 0°. The amide forms quadratic needles, $a : c = 1 : 2{\cdot}1505$. Γ^{cis} Δ^2 *Tetrahydroterephthalic acid* is soluble in 37 parts of cold water, and melts between 150° and 155°. The barium, cadmium, and silver salts are amorphous. The methyl salt is a liquid. In their chemical behaviour, the two geometrical isomerides exhibit the closest possible resemblance; they are both converted into Δ^1 tetrahydroterephthalic acid by boiling with sodium hydroxide solution.

The following table shows the solubility of the different acids, and it also gives the melting points of the methyl salts of these acids :—

	Parts of cold water required to dissolve 1 part of acid.	M. p. of methyl salt.
Hexahydroterephthalic acid........	1,000	71°
Δ^1 tetrahydroterephthalic acid (1α-position)	4,000	39°
Δ^2 tetrahydroterephthalic acid (1β-position)	600	about 3°
$\Delta^{1:3}$ dihydroterephthalic acid (2α-positions)	19,000	85°
$\Delta^{1:4}$ dihydroterephthalic acid (2α-positions)	17,000	130°
$\Delta^{1:5}$ dihydroterephthalic acid (1α- and 1β-position)	2,400	40°
$\Delta^{2:5}$ dihydroterephthalic acid (2β-positions)	300	77°
Terephthalic acid..................	67,000	140°

It appears from this table that a double linking in the α-position diminishes, and a double linking in the β-position increases the solubility of the acid in water. The α-position tends to raise and the β to lower the melting point of the methyl salts of these acids. The constitutional formula for benzene proposed by Claus is no longer tenable in the light of the results of this research; but the new facts can be explained either by Dewar's, Kekule's, or the central formula for benzene. The author now withdraws his objection to Kekule's benzene formula, which was based on the resistance benzene offered to oxidation with permanganates, as he finds that the double linking in phenanthrene resists oxidation by permanganate, whilst the double linking in stilbene does not. W. C. W.

Action of Phosphorus Pentachloride on Ethyl Succinosuccinate. By S. Levy and A. Curchod (*Ber.*, **22**, 2106—2114).—In addition to paradichlorodihydroterephthalic acid (compare Abstr., 1888, 840), dihydroxyterephthalic acid is also formed by the action of phosphorus pentachloride on ethyl succinosuccinate, and constitutes about one-third of the product.

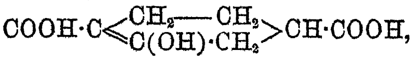
Paradichloroterephthalic chloride, $C_6H_2Cl_2(COCl)_2$, is obtained when a mixture of paradichlorodihydroterephthalic acid with 2 molecular proportions of phosphorus pentachloride is allowed to remain in the cold until the evolution of hydrogen chloride has ceased, and then heated in a water-bath for about six hours to complete the reaction. The resulting chlorides of phosphorus are removed by distillation, and the residual syrupy liquid heated at 275—295°, at which temperature decomposition takes place with the elimination of hydrogen chloride, and a liquid distils over which solidifies in the receiver, and consists of a mixture of paradichloroterephthalic chloride with a very small quantity of an acid readily soluble in water and alkalis, but insoluble in light petroleum. The separation is effected by extracting the chloride with light petroleum, from which it crystallises in colourless, strongly refractive, monoclinic prisms, $a : b : c = 1·8450 : 1 : 2·4024$, $\beta = 101° 55'$, melting at 80·5—81°. The *amide*, $C_6H_2Cl_2(CONH_2)_2$, crystallises from water in colourless needles, does not melt at 300°, is insoluble in benzene and carbon bisulphide, and very sparingly soluble in boiling water.

Methyl paradichloroterephthalate (Abstr., 1888, 1091) is formed when paradichloroterephthalic chloride is warmed with methyl alcohol. It is also obtained when a mixture of methyl paradichlorodihydroterephthalate with 2 molecular proportions of phosphorus pentachloride is digested on a water-bath for about eight hours, then heated at a higher temperature to remove the chlorides of phosphorus by distillation, and finally further heated at 270°, at which temperature the methyl salt distils over and can be purified by crystallisation from light petroleum. Prepared in either of these ways, it is found to melt at 136°, and not at 131—132° as previously stated (*loc. cit.*).

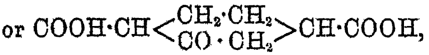
When paradichlorodihydroterephthalic acid (10 grams), dissolved in the requisite quantity of aqueous soda of sp. gr. = 1·12 and the solution diluted with water (100 c.c.), is treated with 4 per cent. sodium amalgam (170 grams) in large pieces at a time, it is reduced to Baeyer's $\Delta^{1,4}$ dihydroterephthalic acid (Abstr., 1888, 1072; compare preceding Abstract). The yield of this acid is greatly influenced by the duration of the reduction, the best yield, about one-sixth part of the paradichlorodihydroterephthalic acid employed, being obtained when the reduction is effected as rapidly as possible by introducing the whole of the amalgam at once into the alkaline solution of the chlorinated acid. Salicylic acid and a chlorinated compound which has not yet been obtained in a state of purity are also formed in the reduction of the chlorinated acid. W. P. W.

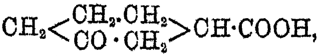
Reduction-products of Hydroxyterephthalic Acid. By A. BAEYER and F. TUTEIN (*Ber.*, **22**, 2178—2189).—Terephthalic acid is best prepared by converting paratoluidine into the corresponding nitrile by Sandmeyer's method, hydrolysing this with sulphuric acid diluted with one-third its volume of water, and oxidising the resulting paratoluic acid with a 10 per cent. solution of potassium permanganate. The conversion into hydroxyterephthalic acid is best effected by a modification of Burckhard's method (this Journal, 1877, ii, 336), terephthalic acid (20 grams) being nitrated with a mixture of fuming nitric acid free from nitrous acid (150 grams) and ordinary fuming sulphuric acid (225 grams), the nitro-acid (20 grams) reduced by suspending it in concentrated hydrochloric acid and adding tin (20 grams); the amido-acid produced is then diazotised and boiled with water, and the resulting hydroxyterephthalic acid purified by conversion into its dimethyl salt which is finally saponified with dilute aqueous soda.

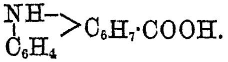
Tetrahydrohydroxyterephthalic acid,



$$\mathrm{COOH{\cdot}C}\begin{matrix}\diagup\mathrm{CH_2{-\!\!-}CH_2}\diagdown\\ \diagdown\!\!\diagdown\mathrm{C(OH){\cdot}CH_2}\diagup\end{matrix}\mathrm{CH{\cdot}COOH},$$

or  $\mathrm{COOH{\cdot}CH}\begin{matrix}\diagup\mathrm{CH_2{\cdot}CH_2}\diagdown\\ \diagdown\mathrm{CO{\cdot}CH_2}\diagup\end{matrix}\mathrm{CH{\cdot}COOH}$, is obtained when a solution of hydroxyterephthalic acid (2 grams) in the requisite quantity of aqueous soda is diluted with 30 to 40 times its volume of water, cooled in ice and treated with 3 per cent. sodium amalgam (40 grams) until it is no longer fluorescent, and is not precipitated on acidification with dilute sulphuric acid; the acidified solution is then extracted with ether, and the ethereal solution concentrated to the crystallising point. The yield amounts to more than 50 per cent. of that theoretically possible. It crystallises in pale yellow, granular crusts, is readily soluble in alcohol, ether, and aqueous sodium carbonate, less soluble in cold water, gives a bluish-violet colour with ferric chloride, and decomposes with the evolution of carbonic anhydride when boiled with water. The *methyl* salt, $C_6H_8O(COOMe)_2$, crystallises in stellate groups of feathery needles, melts at 75—77°, is soluble in methyl alcohol, chloroform, and aqueous alkaline carbonates, and yields a violet colour on addition of ferric chloride to its solution.

Metaketohexahydrobenzoic acid,  $\mathrm{CH_2}\begin{matrix}\diagup\mathrm{CH_2{\cdot}CH_2}\diagdown\\ \diagdown\mathrm{CO{\cdot}CH_2}\diagup\end{matrix}\mathrm{CH{\cdot}COOH}$, is formed when tetrahydrohydroxyterephthalic acid is heated at 115—120°, but could not be obtained in a crystalline form. Its solution in water is not coloured by the addition of ferric chloride. The *sodium* salt, $C_6H_9O{\cdot}COONa$, obtained by boiling an aqueous solution of tetrahydrohydroxyterephthalic acid until the evolution of carbonic anhydride ceases, and then neutralising with sodium carbonate, crystallises in very hygroscopic, slender needles. The *oxime*, $C_7H_{10}O_2{:}N{\cdot}OH$, prepared by adding powdered tetrahydrohydroxyterephthalic acid to a concentrated solution of hydroxylamine hydrochloride, and gently warming until the evolution of carbonic anhydride ceases, forms small, colourless, regular crystals, melts at 170° with decomposition, and is soluble in hot water and alkaline carbonates. The *phenylhydrazone*, $C_7H_{10}O_2{\cdot}N_2HPh$, formed by adding powdered tetrahydrohydroxyterephthalic acid to an aqueous solution of phenylhydrazine, and heating in a water-bath until carbonic anhydride is no longer evolved, is a bright yellow, finely granular powder, melts at 125°, is readily soluble in alkaline carbonates, does not form an azo-compound but is resinified on treatment with alcoholic ferric chloride, and when warmed with mineral acids loses a molecular proportion of ammonia and is converted into *tetrahydrocarbazolecarboxylic acid*,



$$\left.\begin{array}{l}NH-\\ |\\ C_6H_4\end{array}\right>C_6H_7{\cdot}COOH.$$

This compound melts at 230°, is crystalline, dissolves in alkaline carbonates, and decomposes when heated above its melting point with the formation of products which have a fæcal odour, and give a red colour to a pine-shaving moistened with hydrochloric acid. The *cyanhydrin*, $C_7H_{11}O_3{\cdot}CN$, prepared by treating a mixture of ketohexahydrobenzoic acid and potassium cyanide cooled in a freezing mixture with fuming hydrochloric acid, crystallises in colourless, hard, monoclinic prisms, melts at 130—140°, is soluble in alcohol and ether, and when saponified with concentrated hydrochloric acid is converted into the corresponding *metadicarboxylic acid*, $C_6H_8O(COOH)_2$, which forms hard, granular crystals, and is soluble in alcohol.

Benzoxyterephthalic acid, $CH_2Ph{\cdot}O{\cdot}C_6H_3(COOH)_2$, is obtained by boiling an alcoholic solution of benzyl chloride and the sodium salt of methyl hydroxyterephthalate in molecular proportion for six hours, and saponifying the resulting methyl benzoxyterephthalate with a solution of potassium hydroxide in methyl alcohol. It crystallises in lustrous, slender needles, melts at 230—240°, is soluble in alcohol and insoluble in water, and does not give a colour reaction when treated with ferric chloride. W. P. W.

Paracarboxyhydrocinnamic Acid. By O. WIDMAN (*Ber.*, 22, 2272—2274).—*Paracarboxyhydrocinnamic acid*,

$$COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained when cumenylpropionic acid is boiled with a mixture of nitric acid (sp. gr. = 1·2) with twice its volume of water until completely dissolved. It crystallises in small, colourless nodules, melts at 277—278° with sublimation, and dissolves slowly but in large quantity in boiling water and alcohol. On nitration with a mixture of 10 parts of fuming nitric acid and 20 parts of concentrated sulphuric acid, it yields *nitroparacarboxyhydrocinnamic acid*, $COOH.C_6H_3(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ [$COOH : NO_2 : CH_2{\cdot}CH_2{\cdot}COOH = 1 : 3 : 4$], which melts at 191—192°, does not crystallise well, and is readily soluble in methyl and ethyl alcohols, and in boiling water and 50 per cent. acetic acid, but is insoluble in benzene.

Hydrocarbostyrilcarboxylic acid, $C_9H_8NO{\cdot}COOH$ [COOH = 2], is prepared by reducing the nitro-acid with ferrous sulphate. It crystallises in lustrous scales, melts at about 280°, and is insoluble in boiling benzene, and very sparingly soluble in boiling methyl or ethyl alcohol or boiling water. Its *methyl*-salt, $C_9H_8NO{\cdot}COOMe$, forms large, yellow crystals, or thick tetragonal tables, melts at 191—192°, and is sparingly soluble in boiling alcohol.

W. P. W.

Constitution of Cumenylpropionic Acid. By O. WIDMAN (*Ber.*, **22**, 2266—2272).—In a previous paper (Abstr., 1887, 132), the author has indicated the arguments which lead him to believe that cumenylpropionic acid contains a normal propyl-group, and the present experiments have been undertaken with the view of preparing the isomeric acid in order that this point may be decided by a comparison instituted between the two isomerides.

Cuminalmalonic acid, $CHMe_2{\cdot}C_6H_4{\cdot}CH{:}C(COOH_2)$, is prepared by heating a mixture of cumaldehyde (2 parts), malonic acid (2 parts), and acetic acid (1 part) for 10 hours at 100°; the excess of malonic acid crystallises out and can be separated from the oil, which is then shaken with aqueous soda, treated with ether to extract the unattacked cumaldehyde, and the alkaline solution precipitated by addition of hydrochloric acid. When anhydrous it melts at 137° without decomposition, is very soluble in methyl and ethyl alcohol and acetic acid, very sparingly soluble in cold benzene and cold water, and decomposes into cumaldehyde and malonic acid when boiled with water. When dissolved in warm water, it readily forms a *hydrate*, $C_{13}H_{14}O_4 + H_2O$, which crystallises in long, white prisms, melts at 89—90°, loses its water of crystallisation at 80—90°, but not when placed in a desiccator at the ordinary temperature, and crystallises unchanged from benzene. Cuminalmalonic acid also combines with benzene, forming the compound $C_{13}H_{14}O_4 + C_6H_6$; this crystallises from benzene in small, slender needles, melts at 96—97°, and readily loses its benzene of crystallisation on exposure to the air. When the anhydrous acid is heated at 160°, carbonic anhydride is evolved and cumenylacrylic acid formed. On reduction with sodium amalgam, cuminalmalonic acid is converted into *cumylmalonic acid*, $C_3H_7{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(COOH)_2$, which crystallises in rhombic tables or in thin scales, melts at 165°, is extremely soluble in alcohol, readily soluble in warm and sparingly soluble in cold water, insoluble in benzene, and is converted into the known cumenylpropionic acid (m. p. = 75·5°) with the loss of carbonic anhydride when heated at 175°.

Ethyl cumylmalonate, $C_3H_7{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(COOEt)_2$ is obtained as a colourless aromatic oil, by treating ethyl malonate (5 grams) with alcoholic sodium ethoxide (0·7 gram sodium in 20 grams of alcohol) and cumic chloride (5·2 grams) by Conrad's method (*Annalen*, **204**, 174). On saponification with aqueous soda (sp. gr. = 1·25), it yields cumylmalonic acid (m. p. = 165°), which when heated at 170° yields the known cumenylpropionic acid (m. p. = 75·5°) and carbonic anhydride.

Ethyl cumylacetoacetate, $C_3H_7\cdot C_6H_4\cdot CH_2\cdot CHAc\cdot COOEt$, prepared by the action of cumic chloride on ethyl sodacetoacetate, boils at 280—300°, and when heated at 100° for several hours with concentrated aqueous potash, yields cumylacetone and the known cumenylpropionic acid (m. p. = 74°), of which the former can be extracted from the product by shaking with ether.

Cumylacetone, $C_3H_7\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COMe$, has a pleasant, flower-like odour, boils at 260—265° (corr.) under a pressure of 758 mm., and is converted into cumic acid when oxidised in very dilute solution with the calculated quantity of potassium permanganate in the cold. The *oxime*, $C_3H_7\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CMe{:}N\cdot OH$, crystallises from light petroleum in long, lustrous prisms, and melts at 56—57°.

W. P. W.

Reduction of Orthosulphobenzoic Chloride. By A. DELISLE (*Ber.*, **22**, 2205—2206).—On reduction with zinc-dust and sulphuric acid, orthosulphobenzoic chloride is converted into *orthohydrothiobenzoic acid*, $SH\cdot C_6H_4\cdot COOH$. This forms a white, amorphous powder, which is sparingly soluble in hot water, readily soluble in alcohol, and is not volatile with steam. The *silver* salt, $SAg\cdot C_6H_4\cdot COOH$, was prepared.

W. P. W.

Orthophenolsulphonic Acid. By J. ALLAIN-LE-CANU (*Compt. rend.*, **109**, 225—228, and 306—308).—The best method of preparation is to add well-cooled sulphuric acid drop by drop to phenol cooled at −10°, and allow to return slowly to the ordinary temperature, the flask being closed to prevent absorption of moisture. After 8 to 10 hours, combination is complete, and the liquid is poured into water and neutralised with barium carbonate; the filtered liquid is then precipitated with potassium hydrogen carbonate, and the filtrate carefully concentrated on a water-bath.

Potassium orthophenolsulphonate crystallises with 2 mols. H_2O in rhombic prisms, elongated along 110, 110, the faces observed being 110, 100, 010, 111, and the parameters 2·103 : 1·660 : 1. The plane of the optical axes is parallel with 010, and the crystals are negative. Potassium paraphenolsulphonate crystallises in the same system, but the crystals are positive.

In order to obtain the barium salt, the potassium was removed by hydrofluosilicic acid, and the free acid was neutralised with barium carbonate. The barium salt crystallises with 1 mol. H_2O, and dissolves in four times its weight of boiling water; the barium salt of the para-derivative dissolves in twice its own weight of boiling water, and this difference of solubility may be utilised for their separation.

The free acid is obtained by the action of sulphuric acid on the barium salt, the solution being evaporated in a vacuum at the ordinary temperature. It crystallises with 1·5 mols. H_2O and melts at 50° with partial decomposition.

The action of bromine-vapour on potassium orthophenolsulphonate at −5° to −10°, yields a mixture of monobromo- and dibromo-derivatives, which can be separated and purified by crystallisation from water and alcohol. Potassium monobromorthophenolsulphonate crystallises in white needles, soluble in 3 parts of warm water and 10 parts of boiling alcohol. Potassium dibromorthophenolsulphonate forms long, silky needles, which dissolve in 10 parts of boiling water and in 30 parts of boiling alcohol.

Heat of dissolution of potassium orthophenolsulphonate,

$$OH\cdot C_6H_4 : SO_3K,2H_2O = -9\cdot719 \text{ Cal.};$$

the action of potassium hydroxide on the solution develops +7·650 Cal., or practically the same thermal disturbance as in the corresponding reaction with phenol.

Heat of dissolution of barium orthophenolsulphonate at 20·7° = 2 × −6·767 Cal. Treatment of this salt with sulphuric acid leads to the conclusion that—

$$(OH\cdot C_6H_4,SO_3)_2Ba \text{ diss.} + 2BaOH \text{ diss., develops } + 13\cdot5 \times 2 \text{ Cal.}$$

The heat of neutralisation of the free acid by potassium hydroxide develops +13·070 Cal. for the first equivalent, and +7·513 for the second equivalent. A comparison of the following heats of neutralisation—

	Paraphenolsulphonic acid by NaOH.	Aseptole by NaOH.	Orthophenolsulphonic acid by KOH.
1st Equivalent	13·439	13·708	13·070
2nd Equivalent......	8·960	8·561	7·513

shows that in the para- and ortho-derivatives the heat of neutralisation of the first acid function is practically the same, whilst the heat of neutralisation of the second function is greater in the first case. It seems that "aseptole" is a mixture of paraphenolsulphonic acid with a small quantity of the ortho-derivative.

Monobromorthophenolsulphonic acid was obtained from the potassium salt by converting the latter into the lead salt, which was then decomposed by hydrogen sulphide. Heat of neutralisation by sodium hydroxide, 1st equivalent. +13·880 Cal. at 17·5°; 2nd equivalent, +10·623 Cal. The substitution of bromine for hydrogen increases the heat of neutralisation of the second acid function, and a comparison of these numbers with the corresponding values for the para-derivative, +13·520 and +10·703 Cal. respectively, shows that in both derivatives the substitution of bromine has practically no influence on the heat of neutralisation of the first acid function, and that the increase in the value of the second function is nearly the same in both cases. C. H. B.

Iodophenolsulphonic Acids and Iodoquinones. A Second Iodothymoquinone. By F. KEHRMANN (*J. pr. Chem.* [2], **40**, 188—189; compare this vol., p. 993).—Carvacrolparasulphonic acid yields an *iodo-derivative*, [OH : Me : SO_3H : Pr : I = 1 : 2 : 4 : 5 : 6], which is converted into iodothymoquinone by gradually adding a slight excess of a dilute sulphuric acid solution of chromic acid to a dilute sulphuric acid solution of its crystalline potassium salt.

Iodothymoquinone [O_2 : Me : Pr : I = 1 : 4 : 2 : 5 : 6] crystallises from alcohol in large, garnet-red plates, melts at 65—66°, and is more readily soluble in alcohol, ether, &c., and more volatile than the isomeric compound previously described (*loc. cit.*). It combines with hydroxylamine hydrochloride in alcoholic solution, but much more slowly than does the isomeride. F. S. K.

Phenoldisulphonic Acid. By J. ALLAIN-LE-CANU (*Compt. rend.*, **109**, 442—444).—Separate vessels containing sulphuric acid of sp. gr. 1·84—1·85 and phenol were allowed to remain in a vacuum for six months. The semi-solid crystalline product contained in the vessel which formerly contained the sulphuric acid, was dissolved in water and treated with barium carbonate, and the filtrate precipitated with potassium hydrogen carbonate. On concentration, the second filtrate yielded lamellar crystals of potassium phenoldisulphonate, and acicular crystals of potassium paraphenolsulphonate. No orthophenolsulphonate was obtained, and it follows that the sulphuric acid combines most readily with the ortho-mono-derivative, probably in consequence of its well-known tendency to take the para-position.

Potassium phenoldisulphonate crystallises with 2 mols. H_2O, becomes anhydrous at 200°, dissolves in three parts of boiling water, and decomposes without melting at about 270°. *Barium phenoldisulphonate* crystallises readily, and is easily separated from the paraphenolsulphonate. It crystallises with 4 mols. H_2O from a warm solution in short bulky crystals and from a cold solution in long needles, which become anhydrous at 160°; the heat of dissolution at 20—21° is − 7·888. Decomposition by sulphuric acid develops +27·3 Cals., double the number obtained with the orthophenolsulphonate. The free acid may be obtained from the barium salt; its heat of neutralisation by three successive equivalents of sodium hydroxide are +13·315 Cal., +13·386 Cal., and +9·276 Cal. The second substitution of the sulphonic-group increases the energy of the third acid function in the same manner as the substitution of bromine, but has practically no effect on the first acid function. It is known that the heat of neutralisation of the sulphonic group is almost the same, whether it is in the ortho- or para-position, and the behaviour of phenoldisulphonic acid shows that it is not affected by its simultaneous occurrence in both positions. C. H. B.

Isomeric Change in the Propyl-group. By O. WIDMAN (*Ber.*, **22**, 2274—2280).—*Metasulphocumic acid*,

$$CHMe_2\cdot C_6H_3(SO_3H)\cdot COOH[COOH : SO_3H : CHMe_2 = 1 : 3 : 4],$$

is obtained by treating powdered cumic acid with an equal weight of sulphuric anhydride. It is crystalline, and readily soluble in water, and melts at about 160°. The *barium* salt, with 1 mol. of H_2O, is moderately soluble in hot and cold water, yielding a solution devoid of fluorescence; the *barium hydrogen* salt, $(C_{10}H_{11}O_2\cdot SO_3)_2Ba + 4\frac{1}{2}H_2O$, crystallises in long, lustrous prisms, is more soluble in hot than in cold water, and gives solutions showing a strong yellowish-green fluorescence. The *dichloride*, $CHMe_2 \cdot C_6H_3(SO_2Cl) \cdot COCl$, crystallises from light petroleum in large, strongly-refractive prisms, melts at 55—56°, and is not decomposed by prolonged boiling with water; the *diamide*, $CHMe_2 \cdot C_6H_3(SO_2NH_2) \cdot CONH_2$, crystallises from water in rhombic tables, melts at 225°, and in the cold forms salts with potassium hydroxide and the strongest bases without the evolution of ammonia. When heated on the water-bath with aqueous potash (sp. gr. = 1·30) until ammonia is no longer evolved, the diamide is converted into sulphonamidocumic acid $CHMe_2 \cdot C_6H_3(SO_2NH_2) \cdot COOH$; this crystallises in long, lustrous needles, melts at 246° (corr.), and is identical with Remsen and Day's α-sulphonamidopropylbenzoic acid (Abstr., 1884, 456). It follows, therefore, that an isomeric change from normal to iso-propyl takes place during the oxidation of the methyl group of β-cymenesulphonamide to carboxyl.

Metasulphopropylbenzoic acid,

$$SO_3H \cdot C_6H_3Pr \cdot COOH, [COOH : SO_3H : Pr = 1 : 3 : 4],$$

is prepared by shaking acetopropylbenzene (4 grams) with a solution of potassium permanganate (7·8 grams) and potassium hydroxide (3·2 grams) in water (1 litre), allowing the whole to remain for 12—24 hours until decolorised, filtering from the separated manganese oxide, acidifying with hydrochloric acid and extracting with ether. The acid does not crystallise well, has not a sharp melting point, and is readily soluble in alcohol, ether, and water, but insoluble in benzene. The *barium* salt, with 1 mol. H_2O, crystallises in long prisms or spear-like needles, and is somewhat sparingly soluble in warm and cold water. The *dichloride*, $SO_2Cl \cdot C_6H_3Pr \cdot COCl$, forms prismatic crystals, melts at 42—43°, and is very soluble in benzene and light petroleum; the *diamide*, $NH_2 \cdot SO_2C_6H_3Pr \cdot CONH_2$, crystallises from water in well-formed, rhombic tables, and melts at 202—203°. Sulphonamidopropylbenzoic acid, $NH_2 \cdot SO_2 \cdot C_6H_3Pr \cdot COOH$, crystallises from water in long needles, and melts at 216° (corr.) when introduced in the solid form into the melting point tube, and at 218° (corr.) when the fused specimen, after solidification in the tube, is again heated for the melting point determination. This acid, in spite of the somewhat higher melting point, is undoubtedly identical with the β-sulphonamidopropylbenzoic acid obtained by Remsen and Keiser (Abstr., 1884, 457) by the oxidation of diparapropylbenzenesulphonamide under conditions similar to those employed in the oxidation of β-cymenesulphonamide. It follows, therefore, that the isomeric change from normal to iso-propyl is not exclusively conditioned by the presence of the carboxyl-group or by the process of oxidation adopted, but depends largely on the nature of the group which undergoes oxidation to carboxyl. W. P. W.

Synthesis of Symmetrical Diphenylsulphoneacetone by means of Tetrachloracetone. By R. OTTO (*Ber.*, **22**, 1965—1968; compare R. and W. OTTO, Abstr., 1888, 282).—Diphenylsulphoneacetone can be prepared by heating symmetrical tetrachloracetone hydrate with sodium benzenesulphinate (4 mols.) in dilute alcoholic solution. The yield is very small. F. S. K.

Indole-derivatives. By G. CIAMICIAN and C. ZATTI (*Ber.*, **22**, 1976—1982).—Indole can be readily prepared by distilling calcium 2′-indolecarboxylate with calcium oxide; the yield is about 50 per cent. of the calcium salt employed. (Compare Mauthner and Suida, Abstr., 1889, 1069.) It melts at 52·5°, and boils at 253—254° (corr. 762·2 mm.). When calcium 2′-indolecarboxylate is distilled with calcium formate, indole alone is obtained; pyrroline-α-carboxylic acid behaves in a a similar manner.

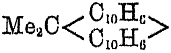
A solution of indole in concentrated sulphuric acid gives an intense carmine coloration with isatin; with alloxan, under the same conditions, a transient emerald-green coloration is produced, and with benzil, on warming, a yellowish-brown coloration. Indole is insoluble in cold hydrochloric acid, and, on heating, is converted into a reddish-yellow, resinous mass, readily soluble in alcohol. In the alcoholic solution, water produces a white precipitate which, on boiling, cakes together to a soft, yellowish mass.

When indole is heated at 180—200° with acetic anhydride, it yields 1′,3′-diacetylindole and small quantities of 3′-acetylindole; these compounds are identical with the acetyl-derivatives prepared by Baeyer (Abstr., 1879, 937).

1′,3′-Diacetylindole is converted into 3′-acetylindole when it is boiled with sodium carbonate.

When indole (1 part) is heated at 130° for eight hours with methyl iodide (6 parts), methyl alcohol (1·5 parts), and sodium carbonate (1 part), dimethyldihydroquinoline is formed, identical with the compound obtained by Fischer and Steche (Abstr., 1888, 298) from methylketole. F. S. K.

Condensation-products of Acetone and its Homologues with Phenol. By A. P. DIANIN (*J. Russ. Chem. Soc.*, 1888, 534—535, and 656—657).—The condensation-product of acetone with phenol in presence of benzoic chloride crystallises in glistening, feathery, flat needles melting at 153·6° (corr.); this the author considers to be *dimethyldiphenolmethane*, $CMe_2(C_6H_4{\cdot}OH)_2$. The higher homologues of acetone readily react with phenol in the presence of hydrochloric acid; thus diethyl ketone and phenol give *diethyldiphenolmethane*, $CEt_2(C_6H_4{\cdot}OH)_2$, crystallising in tetragonal four- or six-sided prisms which melt at 198—200°, whilst methyl hexyl ketone with phenol yields *methylhexyldiphenolmethane*, $C_6H_{13}{\cdot}CMe(C_6H_4{\cdot}OH)_2$, in the form of needles which melt at 83·5°. With benzoic chloride, a product of the formula $C_6H_{13}{\cdot}CMe(C_6H_4{\cdot}OBz)_2$, is obtained in the form of needles melting at 114°. The above reaction is very characteristic for ketones.

When dimethyldiphenolmethane is fused with caustic soda, and the product decomposed with sulphuric acid and distilled with steam, it yields a crystalline phenol (m. p. 61°, b. p. 227—228°) identical with the paraisopropylphenol of Paternò and Spica; so that the parent compound must be dimethyl*para*diphenylmethane. On fusing diethyldiphenolmethane, $CEt_2(C_6H_4{\cdot}OH)_2$, with caustic soda, a crystalline phenol is obtained having the formula $C_5H_{11}{\cdot}C_6H_4{\cdot}OH$. This melts at 76·5° and boils at 253°, and, judging by analogy, should belong to the para-series. A better yield of this phenol is obtained by heating diethyldiphenolmethane with fuming hydrochloric acid at 110° or by heating a mixture of diethyl ketone and phenol with fuming hydrochloric acid at 100°. When acetone is heated with α-naphthol in presence of hydrochloric and acetic acids, tetragonal scales of *dimethyloxydinaphthylenmethane*,  $Me_2C<\genfrac{}{}{0pt}{}{C_{10}H_6}{C_{10}H_6}>O$, are obtained; it melts at 186°. With β-naphthol no reaction was obtained under the same conditions. B. B.

Condensation-products of Benzaldehyde with Phenol and Thymol. By A. Russanow (*Ber.*, **22**, 1943—1949).—Paradihydroxytriphenylmethane is formed, but only very slowly, when benzaldehyde is treated with phenol in presence of a small quantity of dilute sulphuric acid; when heated with bromine-water, it yields a compound the alcoholic solution of which turns blue on the addition of a little alkali. The *diacetyl*-derivative, $CHPh(C_6H_4{\cdot}OAc)_2$, crystallises from aqueous acetone in rhombic plates, melts at 109—111°, and is soluble in all the ordinary solvents. The *dibenzoyl*-derivative, $CHPh(C_6H_4{\cdot}OBz)_2$, crystallises from alcohol in microscopic plates, melts at 129—130°, and is readily soluble in all the ordinary solvents except alcohol. The *dinitro*-compound, $C_{19}H_{14}O_2(NO_2)_2$, prepared by treating dihydroxytriphenylmethane with nitric acid in glacial acetic acid solution, crystallises from alcohol in slender, yellow needles, melts at 133—134°, and is soluble in dilute acetic acid and in alkalis.

Dithymolphenylmethane, $CHPh(C_{10}H_{13}O)_2$, is obtained when dilute sulphuric acid is gradually added to a mixture of benzaldehyde (1 mol.) and thymol (2 mols.). 20 grams of benzaldehyde yield 68 grams of the product. It crystallises from 80 per cent. alcohol with 1 mol. of alcohol, and from benzene with $\frac{1}{2}$ mol. of benzene in rhombic plates, melts at 145·5—146·5°, and is readily soluble in chloroform, light petroleum, and acetic acid; it dissolves in alkalis yielding a colourless solution, which is turned green by potassium permanganate, and with bromine water it gives the same reaction as dihydroxytriphenylmethane. The *diacetyl*-derivative, $CHPh(C_{10}H_{12}{\cdot}OAc)_2$, separates from alcohol in small, rhombic crystals, melts at 125—126°, and is readily soluble in chloroform, benzene, acetone, and acetic acid.

F. S. K.

Derivatives and Reactions of Tetramethyldiamidobenzophenone. By M. Nathansohn and P. Müller (*Ber.*, **22**, 1875—1901).—*Dibenzoyldimethyldiamidobenzophenone*, $CO(C_6H_4{\cdot}NMeBz_2)_2$, prepared by heating tetramethyldiamidobenzophenone with excess of benzoic chloride at 190°, crystallises from alcohol in brownish plates, melts at 102°, and is readily soluble in hot alcohol, but only sparingly in hot benzene, and almost insoluble in ether and water. It is not decomposed by acids or alkalis at 100°, but at higher temperatures a resinous compound is formed.

Tetramethyldiamidobenzophenone methiodide, $CO(C_6H_4{\cdot}NMe_3I)_2$, prepared by heating the ketone with methyl iodide and methyl alcohol at 110—120°, crystallises from alcohol in light-yellow plates, melts at

105°, and is readily soluble in hot alcohol and hot water, but only sparingly in benzene and ether; it is decomposed when heated to 150°. When the aqueous solution is digested with silver oxide, silver iodide separates, and the filtrate, on evaporation, yields the *hydroxide* as a yellowish-brown, crystalline, deliquescent, unstable compound; the *hydrochloride* and the *platinochloride* of the hydroxide are also unstable.

Tetramethyldiamidobenzhydrol, $CH(C_6H_4 \cdot NMe_2)_2 \cdot OH$, is formed when the ketone is reduced with sodium amalgam in warm alcoholic solution. (Compare Michler and Dupertius, this Journal, 1877, ii, 333.) It crystallises from ether or benzene in colourless prisms, melts at 96°, and is readily soluble in hot alcohol and glacial acetic acid. The *hydrochloride*, $C_{17}H_{22}N_2O,HCl$, crystallises from alcoholic ether in small, deliquescent, colourless needles, is decomposed by water, and turns first green and then blue on exposure to the air. The *platinochloride*, $C_{17}H_{22}N_2O,H_2PtCl_6$, crystallises in microscopic, yellow needles, is readily soluble in alcohol, and turns blue on exposure to the air. The *picrate*, $C_{17}H_{22}N_2O,C_6H_3N_3O_7$, is a dark-green compound, readily soluble in hot alcohol but only sparingly in benzene, and insoluble in ether. The *methiodide*, $CH(C_6H_4 \cdot NMe_3I)_2 \cdot OH$, crystallises from alcohol in almost colourless plates, melts at 195°, is decomposed at about 240°, and is readily soluble in hot alcohol and water, but almost insoluble in benzene and ether.

Tetramethyldiamidodiphenylmethane is formed when the ketone is distilled over zinc-dust in an atmosphere of hydrogen.

Tetramethyldiamidotetrabromobenzophenone, $CO(C_6H_2Br_2 \cdot NMe_2)_2$, prepared by treating the ketone with excess of bromine in glacial acetic acid solution, crystallises from alcohol in small, yellowish needles, melts at 172°, and is sparingly soluble in benzene and ether, but readily in hot alcohol.

Tetramethyldiamidonitrobenzophenone,

$$NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_3(NO_2) \cdot NMe_2,$$

prepared by treating the ketone with a mixture of sulphuric acid and nitric acid, crystallises from alcohol in small, bright-yellow needles, melts at 144°, and is readily soluble in hot alcohol and benzene, but only sparingly in ether.

Tetramethyltriamidobenzophenone, $NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_3(NH_2) \cdot NMe_2$, prepared by reducing the preceding compound with hydrochloric acid and stannous chloride, is best obtained in a pure state by decomposing the picrate with ammonia. It is a yellowish-brown powder, melts at 82°, and is readily soluble in boiling alcohol and benzene, but almost insoluble in ether. The *picrate*, $C_{17}H_{21}N_3O,C_6H_3N_3O_7$, separates in light-yellow crystals when an alcoholic solution of the base is treated with alcoholic picric acid; it is almost insoluble in benzene and ether, but readily in hot alcohol, from which it crystallises in microscopic plates. The *platinochloride*, $(C_{17}H_{21}N_3O)_2,H_2PtCl_6$, is a light-red, crystalline compound, readily soluble in warm alcohol, but only sparingly in benzene, and insoluble in water and ether.

Tetramethyltriamidotriphenylmethane, prepared by heating tetramethyldiamidobenzhydrol with aniline and hydrochloric acid

(D.R.-P. 27032), crystallises from alcohol in small, almost colourless needles, melts at 65°, and is readily soluble in ether and benzene, but insoluble in water. The *hydrochloride*, $C_{23}H_{27}N_3,2HCl$, is a yellowish-green, crystalline compound, readily soluble in hot alcohol, but only sparingly in ether, and insoluble in benzene. The *platinochloride*, $C_{23}H_{27}N_3,H_2PtCl_6$, is a light-yellow, flocculent compound only sparingly soluble in alcohol and insoluble in water. The *picrate*, $C_{23}H_{27}N_3,C_6H_3N_3O_7$, is a light-green, flocculent substance, readily soluble in hot alcohol, but almost insoluble in benzene and ether. The *benzoyl*-derivative, $CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_4\cdot NHBz$, prepared by heating the base with excess of benzoic anhydride at 150°, crystallises from warm, dilute alcohol in almost colourless plates, melts at 128°, and is readily soluble in hot benzene, but only sparingly in ether, and insoluble in water. The *methiodide*, $CH(C_6H_4\cdot NMe_3I)_3$, crystallises from warm alcohol in small, brownish needles, melts at 172°, and is readily soluble in hot water, but almost insoluble in ether and benzene; it is decomposed at a moderately high temperature. This compound is isomeric with the methiodide of tetramethylparaleucaniline, and, as benzhydrol and aniline hydrochloride yield an orthamidotriphenylmethane, the constitution of tetramethyltriamidotriphenylmethane is $(NMe_2\cdot \overset{4}{C_6H_4})_2\overset{1}{C}H\cdot C_6H_4\cdot\overset{2}{N}H_2$.

Tetramethylnaphthylpararosaniline (Victoria-blue B, D.R.-P. 27789) crystallises from alcoholic benzene in bronze-coloured plates, and is readily soluble in hot water and alcohol, but only sparingly in ether. When heated at 230—250° with concentrated hydrochloric acid, methyl chloride, dimethylaniline, resinous products, and a *ketone*, $C_{23}H_{18}N_2O$, are formed. The ketone is a light-yellow, flocculent substance, melts at 92°, and is very sparingly soluble in alcohol, benzene, and ether, but moderately easily in boiling toluene and cumene, and readily in mineral acids. It is not decomposed by concentrated hydrochloric acid at 300°, or by soda-lime, and its constitution is probably either

$$NH_2\cdot C_6H_4\cdot CO\cdot C_{10}H_6\cdot NHPh \text{ or } NH_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NH\cdot C_{10}H_7.$$

The *platinochloride*, $C_{23}H_{18}N_2O,H_2PtCl_6$, is a yellow, flocculent compound; the *picrate*, $C_{23}H_{18}N_2O,C_6H_3N_3O_7$, is brown.

When tetramethylnaphthylpararosaniline is distilled alone, or with soda-lime, or with zinc-dust in an atmosphere of hydrogen, large quantities of dimethylaniline and phenyl-α-naphthylamine are formed.

The *colour-base*, $C_{33}H_{33}N_3O$, prepared by decomposing the salt with soda, is a reddish-black powder, melts at 95°, and is readily soluble in alcohol and benzene. The *platinochloride*, $(C_{33}H_{31}N_3)_2PtCl_6$, crystallises in violet needles, and is only sparingly soluble in hot alcohol and almost insoluble in ether and benzene. The *picrate*, $C_{33}H_{31}N_3,C_6H_3N_3O_7$, is a dark-blue, flocculent compound. The *leuco-base*, $C_{33}H_{33}N_3$, prepared by reducing the colour-base with zinc and hydrochloric acid, is a light-blue, flocculent compound melting at 125°; it is readily soluble in hot alcohol and ether. The *picrate*, $C_{33}H_{33}N_3,C_6H_3N_3O_7$, crystallises from warm alcohol in greenish plates, and is readily soluble in hot benzene, but only sparingly in ether.

The *platinochloride*, $(C_{33}H_{33}N_3)_2,H_2PtCl_6$, is a light bluish-green compound moderately soluble in hot alcohol, but only sparingly in benzene and ether.

Tetramethylphenylmethyl-α-naphthylamine (Victoria-blue IVR), $C_{34}H_{34}N_3Cl$, resembles tetramethylnaphthylpararosaniline, but has a somewhat brighter, metallic lustre. The *colour-base*, $C_{34}H_{35}N_3O$, is a vermilion, flocculent compound, melts at 77°, and is readily soluble in alcohol, but only sparingly in benzene. The *platinochloride*, $(C_{34}H_{33}N_3)_2,H_2PtCl_6$, and the *picrate*, $C_{34}H_{33}N_3,C_6H_3N_3O_7$, are violet, crystalline compounds, readily soluble in hot alcohol, but only sparingly in benzene and ether. The *leuco-base*, $C_{34}H_{35}N_3$, is a light-blue, flocculent compound, melts at 87°, and is readily soluble in alcohol and ether, but only sparingly in boiling benzene. The *picrate*, $C_{34}H_{35}N_3,C_6H_3N_3O_7$, is a green, flocculent compound, readily soluble in hot alcohol and benzene, but only sparingly in ether. The *platinochloride*, $(C_{34}H_{35}N_3)_2,H_2PtCl_6$ is a light bluish-green compound only sparingly soluble in warm alcohol and ether. F. S. K.

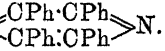
Reduction of Amarine. By G. GROSSMANN (*Ber.*, **22**, 2298—2305).—Zaunschirm has announced that amarine on reduction with sodium yields a peculiar compound melting at 163° (Abstr., 1888, 1077), and the author has identified this with dibenzylidenestilbenediamine. It is best obtained by heating amarine (10 grams) with absolute alcohol (75 grams) in a reflux apparatus on a water-bath, and gradually adding sodium wire (3·5 grams); the syrupy solution is then treated with 50 grams more alcohol and 1·5 grams of sodium, and when the latter is dissolved the whole is poured into 400 c c. of water and the precipitated viscid mass washed with water and then crystallised from alcohol. The yield amounts to 18—20 per cent. of the amarine employed, but a large proportion of amarine is not acted on during the reaction.

Stilbenediamine, $NH_2·CHPh·CHPh·NH_2$, is prepared by boiling Zaunschirm's compound with dilute sulphuric acid, whereby it is decomposed into benzaldehyde and the diamine; the former is then removed from the product by distillation with steam. It crystallises from water or ether in white scales, melts at 120—121°, decomposes to some extent on distillation, and has a molecular weight of 208·9 as determined by Raoult's method in acetic acid solution. The *hydrochloride*, $C_{14}H_{16}N_2,2HCl$, crystallises in white needles and is sparingly soluble in alcohol and cold water; the *platinochloride*, $C_{14}H_{16}N_2,H_2PtCl_6$, forms dark-yellow crystals; the *diacetyl*-compound, $C_{14}H_{14}N_2(OAc)_2$, separates from acetic acid in small, white crystals, melts at a temperature above 350°, and is insoluble in water, ether, benzene, and light petroleum, and only sparingly soluble in alcohol; the *dibenzoyl*-derivative, $C_{14}H_{14}N_2(OBz)_2$, is insoluble in the ordinary solvents and melts at a high temperature. When boiled in alcoholic solution with phthalic anhydride, it yields a compound,

$$C_{22}H_{18}N_2O_2 + \tfrac{1}{2}H_2O,$$

which forms microscopic crystals, melts at 213°, and is sparingly soluble in boiling alcohol.

Dibenzylidenestilbenediamine, CHPh:N·CHPh·CHPh·N:CHPh, is formed by mixing together equal parts of stilbenediamine and benzaldehyde, and completing the reaction by heating at 100° for a short time. It crystallises in pure white needles, melts at 164°, is moderately soluble in alcohol, ether, and light petroleum, readily soluble in benzene and carbon bisulphide, and is identical with the reduction-product of amarine. On further reduction by means of sodium and boiling alcohol, it is converted into *dibenzylstilbenediamine*, $C_{28}H_{28}N_2$, which crystallises from benzene in beautiful, white needles, melts at 153°, and is sparingly soluble in cold alcohol and moderately soluble in ether and light petroleum. When stilbenediamine and benzaldehyde are heated together at a temperature higher than 100°, ditolanazotide (Japp and Wilson, Trans., 1886, 825) is obtained in addition to dibenzylidenestilbenediamine, and it follows therefore that the former has the constitution



$N\begin{matrix} \diagup\!\!\!\!\diagup \text{CPh·CPh} \diagdown\!\!\!\!\diagdown \\ \diagdown \text{CPh:CPh} \diagup \end{matrix}N.$

Stilbenediamine also reacts with other aldehydes; thus with metanitrobenzaldehyde it forms a compound, $C_{28}H_{22}N_4O_4$, crystallising in well-formed, pale-yellow prisms, which melt at 159—161°, and are sparingly soluble in ether and alcohol; with salicylaldehyde it yields a derivative, $C_{28}H_{24}N_2O_2$, crystallising in yellow four- or six-sided scales or tables which melt at 205°, and are sparingly soluble in alcohol; and with cumaldehyde it reacts forming a compound, $C_{34}H_{36}N_2$, which crystallises in thin, lustrous, white, tetragonal scales, melts at 168°, and is sparingly soluble in cold alcohol, readily soluble in ether and benzene.

When stilbenediamine hydrochloride is submitted to dry distillation, a base is obtained having the composition $C_{21}H_{16}N_2$. It crystallises from ether in small, white needles, melts at 230—240°, forms a sparingly soluble *platinochloride*, $(C_{21}H_{16}N_2)_2,H_2PtCl_6 + 1\frac{1}{2}H_2O$, and resembles lophine in its properties.

Furfurine can be reduced when heated in alcoholic solution at 60—65° with sodium, and a compound, $C_{20}H_{16}N_2O_4$, is obtained which crystallises from alcohol in yellow scales, melts at 174°, and decomposes into furfuraldehyde and a base when boiled with dilute sulphuric acid.

W. P. W.

Structure of the Oximido-group in the Isomeric Benzilemonoximes. By K. Auwers and M. Dittrich (*Ber.*, **22**, 1996—2011; compare Auwers and Meyer, this vol., p. 609, and Beckmann, this vol., p. 980). *Benzyl-α-benziloxime*, COPh·CPh:N·OC$_7$H$_7$, is obtained, together with small quantities of a compound free from nitrogen, when benzyl chloride (1 mol.) is added to an alcoholic solution of benziloxime (1 mol.) and sodium ethoxide (1 mol.), and the mixture boiled for about an hour. It crystallises from hot alcohol in compact prisms, melts at 94°, and is moderately easily soluble in benzene, ether, and chloroform, but only sparingly in cold light petroleum and glacial acetic acid. When heated at 100° in a sealed tube for several hours with concentrated hydrochloric acid, or when treated with hydrogen chloride in ice-cold ethereal solution, it is converted into benzyl-γ-benziloxime.

Benzyl-β-benziloxime is obtained, together with a small quantity of a compound free from nitrogen, when β-benzilemonoxime is treated in the same way; it crystallises from alcohol in compact prisms, melts at 114° and exhibits the same behaviour with solvents as the corresponding α-derivative. When heated at 200° for a long time with concentrated hydrochloric acid, it is decomposed into benzile, benzyl chloride, benzoic acid, hydroxylamine hydrochloride, and ammonium chloride; the formation of benzyl chloride in this reaction shows that the original compound is a derivative of α-benzylhydroxylamine.

Benzyl-α- and benzyl-β-benziloxime are both decomposed by boiling hydriodic acid, yielding benzile, benzyl iodide, and ammonium iodide, but not a trace of benzylamine is formed; this decomposition shows that in neither compound is the benzyl-group in direct combination with nitrogen.

When an alcoholic solution of sodium ethoxide (2 mols.) is added, in the course of several hours, to a boiling alcoholic solution of α-benziloxime (1 mol.) and benzyl chloride (2 mols.), benzyl α-benziloxime (m.p. 94°), together with very small quantities of a basic compound melting at 114° are obtained.

β-benziloxime when treated in like manner yields benzyl-β-benziloxime (m.p. 114°), and small quantities of the same basic compound melting at 114°. This basic substance is identical with the anhydro-product obtained from β-benzylhydroxylamine and benzile, and is a true derivative of β-benzylhydroxylamine.

The above experiments show that the two benzilemonoximes are structurally identical derivatives of α-benzylhydroxylamine.

Benzile combines with α-benzylhydroxylamine hydrochloride (1 mol.) or with the free base, in alcoholic solution at the ordinary temperature, yielding benzyl-γ-benziloxime (m.p. 114°), and small quantities of a non-nitrogenous compound melting at about 175°; at higher temperatures, only benzyl-γ-benziloxime is formed.

Benzile does not combine with β-benzylhydroxylamine hydrochloride in alcoholic solution either at the ordinary temperature or at 100°, but at 130° it yields the anhydro-compound (m.p. 114°) and a very small quantity of a nitrogenous substance of higher melting point; the same compounds are formed when benzile is treated with β-benzylhydroxylamine in presence of excess of soda.

The anhydro-compound (m.p. 114°) referred to above has the composition $C_{21}H_{15}NO$; it crystallises from alcohol in broad, flat needles, is readily soluble in ether, but only moderately so in cold alcohol, and it combines with hydrochloric acid to form a salt which is decomposed by cold water. At 150° it is decomposed by hydrochloric acid, yielding benzile, ammonia, and a gas which burns with a green-edged flame; benzyl chloride and hydroxylamine or its derivatives are not formed in the reaction. When heated at 100° with hydriodic acid, not a trace of benzyl iodide is formed.

When benzile is treated with β-benzylhydroxylamine in presence of a little more than the calculated quantity of sodium carbonate, no reaction takes place in the cold, but, on heating for a long time, the anhydro-compound (m.p. 114°) and very small quantities of a substance (benzyl-*i*-benzilmonoxime) melting at 137° are formed.

Benzyl-i-benziloxime, $C_{21}H_{17}NO_2$, crystallises from alcohol in small, slender needles and is moderately easily soluble in alcohol, but only sparingly in ether; it does not combine with hydrochloric acid, and it is insoluble in alkalis. When warmed with excess of hydroxylamine hydrochloride, it gives a compound soluble in alkalis, and when heated at 200° with hydriodic acid it does not yield a trace of benzyl iodide. It is decomposed by concentrated hydrochloric acid at 120°, yielding benzoic acid, benzil, a gas which burns with a green-edged flame, and the hydrochloride of a base, melting at 85°, but not a trace of benzyl chloride, hydroxylamine, β-benzylhydroxylamine, α-benzylhydroxylamine, or ammonia is formed.

The base (m.p. 85°) crystallises in slender needles, is readily soluble in alcohol, and forms a platinochloride.

The experiments described above prove that both the benzilmonoximes contain one and the same oximido-group, N·OH, and with the same degree of certainty as the difference in structure of the oximido-groups in the two benzaldoximes has been proved by Beckmann. F. S. K.

Isomeric Truxillic Acids. By C. LIEBERMANN (*Ber.*, **22**, 2240—2256).—A re-determination of the molecular weights of derivatives of so-called γ-, δ-, and ε-isatropic acids (Abstr., 1888, 1211; this vol., p. 395) by Raoult's method shows that the formulæ hitherto adopted must be doubled, and in order to avoid confusion the author now proposes to term the acids α-, β- and γ-truxillic acids respectively.

Amyl α-truxillate, $C_{18}H_{14}O_4(C_5H_{11})_2$, is obtained by dissolving α-truxillic acid in eight times its weight of fermentation amyl alcohol, saturating the solution with hydrogen chloride, and heating for 5—6 hours at 100°. It crystallises from acetone in beautiful, pointed prisms, melts at 83°, and on hydrolysis with alcoholic potash yields α-truxillic acid. As determined by Raoult's method in acetic acid solution, it has a molecular weight of 442. The values obtained by Raoult's method in acetic acid solution with methyl β-truxillate and methyl γ-truxillate also agree well with that required for the formula, $C_{18}H_{14}O_4Me_2$.

Ethyl hydrogen γ-truxillate, $COOH{\cdot}C_{16}H_{14}{\cdot}COOEt$ is formed, together with ethyl γ-truxillate (compare Drory, next Abstract), by treating an alcoholic solution of γ-truxillic acid with hydrogen chloride, and can be extracted from the product by shaking with aqueous soda. It crystallises in slender, lustrous needles, melts at 171—172°, is readily soluble in alcohol, ether, acetic acid, and benzene, and yields crystalline metallic salts of which the *silver* salt,

$$COOEt{\cdot}C_{16}H_{14}{\cdot}COOAg,$$

was analysed. When heated at 320°, it is converted into a mixture of α-truxillic acid and ethyl α-truxillate.

Methyl β-truxillate (Abstr., 1888, 1211) crystallises in large, transparent, monoclinic prisms, $a:b:c = 0{\cdot}8263:1:2{\cdot}0191$; $\beta = 89°\ 22'$, observed faces, $0P$, $-P$, $+P$, $\frac{1}{2}\grave{P}\infty$, $-\bar{P}\infty$, $+2\grave{P}2$ and $\frac{2}{3}\grave{P}2$.

It has already been shown that α-truxillic acid is converted into γ-truxillic anhydride when heated with acetic anhydride at 210° (this vol., p. 395); further experiments make it clear that the change involved is one from α- to γ-truxillic anhydride, the α-anhydride being formed by the action of the acetic anhydride. α-Truxillic anhydride is completely converted into the γ-compound when heated at 200° for an hour, but does not undergo change at 150°, even after prolonged treatment with acetic anhydride. γ-Truxillic anhydride is not affected by heating at 200° for many hours with acetic anhydride containing some hydrogen chloride. β-Truxillic anhydride does not undergo isomeric change at high temperatures: when heated to 250° it becomes brown and a small quantity of carbonic anhydride is evolved, and at 270° decomposition takes place with a further evolution of carbonic anhydride and formation of a large quantity of cinnamic acid, but no isomeric anhydride could be detected in the product.

The instability of α-truxillic anhydride is not shared by the α-acid, since the latter may be heated at 310° for half an hour, or at 280° in acetic acid solution for 4 hours, or at 260° with hydrochloric acid of sp. gr. = 1·125 for many hours, without undergoing change. Moreover γ-truxillic acid, which remains unchanged at 130°, is completely converted into the α-acid when heated either at 175° or at 260° for 2 hours with ordinary hydrochloric acid, so that it is possible to pass from the α- to the γ-derivatives, or *vice versâ* at will. β-truxillic acid, like its anhydride, does not undergo isomeric change, except on fusion with caustic potash, when it is converted into a new truxillic acid, termed the δ-acid (*vide infra*). The chlorides of the three acids remain unchanged at a temperature of 200°.

The ethereal salts of each of the three acids were originally prepared by saturating the solution of the acid in methyl or ethyl alcohol with hydrogen chloride. The products thus obtained are found to be respectively identical with those formed when the silver salt of each acid is treated with an ethereal solution of methyl or ethyl iodide in the cold or at 100°, or when the chloride of either the α- or β-acid is treated with sodium methoxide or ethoxide at the ordinary temperature, or the anhydride of the γ-acid reacts with the corresponding alcohol at 160°. Variation in the method of preparation of the ethereal salts does not, therefore, bring about isomeric change.

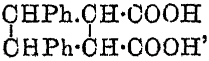
On fusion with caustic potash, α-truxillic acid decomposes with the evolution of hydrogen and production of acetic and benzoic acids together with a third acid, which, however, was not obtained in quantity sufficient to admit of its identification.

δ-Truxillic acid, $C_{18}H_{16}O_4$, is formed when β-truxillic acid is fused with 4 to 5 times its weight of caustic potash. It crystallises from water in beautiful, long, lustrous needles, melts at 174°, yields cinnamic acid on distillation, and is readily soluble in alcohol, sparingly soluble in benzene. It is not attacked by aqueous potassium permanganate in the cold. The *calcium* salt, $C_{18}H_{14}O_4Ca$, crystallises in rosettes of needles, and when once separated from solution is not soluble in water; the *barium* salt crystallises in colourless prisms and is sparingly soluble in boiling water; the *methyl* salt, $C_{18}H_{14}O_4Me_2$, crystallises in lustrous needles, melts at 77°, is readily soluble in alcohol, benzene and light petroleum, gives a molecular weight of 336 by Raoult's method, and yields the unchanged δ-acid on hydrolysis.

Ethyl cinnamate when kept for a long time is converted at the rate of about 2 per cent. per year into a polymeride which forms an insoluble, infusible, chalk-like mass (Erlenmeyer, *Ber.*, **11**, 150). On analysis, the author finds it has the composition

$$(Ph\cdot CH{:}CH\cdot COOEt)x.$$

It decomposes on dry distillation at 300° with the formation of ethyl cinnamate, and differs from the truxillic ethereal salts by its insolubility and infusibility. It is only slightly saponified by treatment with alcoholic potash at 140 or 180°, whilst at 200° it is largely converted into cinnamic acid. When heated with hydrochloric acid of sp. gr. = 1·125 at 200—220° for 12 to 14 hours, it is saponified to a greater extent than with caustic potash, ethyl chloride escapes, and the product on treatment with dilute alkali yields a solution from which an acid insoluble in all solvents can be separated on acidification; this compound is not identical with any one of the isomeric truxillic acids.

The remainder of the paper is devoted to a discussion of the probable formulæ for the isomeric acids. β-Truxillic acid has, probably, the formula  $\begin{array}{l}CHPh.CH\cdot COOH\\ \vert\quad\;\;\;\;\;\vert\\ CHPh\cdot CH\cdot COOH\end{array}$, since it yields both benzil and benzoic acid on oxidation in alkaline solution with 5 per cent. aqueous potassium permanganate; the benzil obtained amounted only to 30 per cent. of that theoretically possible, but this may be accounted for, inasmuch as it would readily be oxidised to benzoic acid under the conditions employed. Further, β-truxillic acid on dry distillation gives not only cinnamic acid but also about 10 per cent. of *dicinnamene*, $C_{16}H_{16}$. This hydrocarbon is formed in very small quantity when ethyl cinnamate is heated in a sealed tube at 300°; it crystallises from alcohol in colourless scales, melts at 124°, and is identical with the compound obtained by distilling cinnamic acid (v. Miller, *Annalen*, **198**, 143), and calcium cinnamate (Engler and Leist, this Journal, 1873, 901). The *dibromide*, $C_{16}H_{16}Br_2$, crystallises from benzene in beautiful needles melting at 238°.

W. P. W.

Salts and Derivatives of the Truxillic Acids. By W. L. Drory (*Ber.*, **22**, 2256—2261).—*Silver α-truxillate*, $C_{18}H_{14}O_4Ag_2$, forms white flocks, and is readily soluble in ammonia; the *barium* salt, with 8½ mols. H_2O, crystallises in large, colourless prisms, and effloresces on exposure to air; the *calcium* salt, with 1 mol. H_2O, is crystalline, and is more soluble in cold than in warm water or 60—70 per cent. alcohol; the *sodium* salt, with 10 mols. H_2O, crystallises in long, colourless prisms, and effloresces on exposure to air. *α-Truxillamide*, $C_{18}H_{18}O_2N_2$, crystallises from alcohol and water in slender, colourless needles, melts at 265°, and is moderately soluble in hot alcohol, very sparingly soluble in hot water.

Barium β-truxillate, $C_{18}H_{14}O_4Ba + 2H_2O$, crystallises in small, thin colourless prisms, and is practically insoluble in water; the *calcium* salt, with 3 mols. H_2O, crystallises in small, white scales, and is insoluble in water; the *sodium* salt, with 2 mols. H_2O, crystallises from 94 per cent. alcohol in very slender, colourless needles. *β-Truxillic chloride*, $C_{18}H_{14}O_2Cl_2$, obtained by the action of phosphorus pentachloride on the acid, crystallises in transparent, rhombic prisms, melts at 96°, is readily soluble in chloroform, benzene, and ether, but sparingly soluble in light petroleum, and when treated with sodium β-truxillate is converted into β-truxillic anhydride.

Silver γ-truxillate forms crystalline flocks; the *barium* salt, with 11 mols. H_2O, crystallises in large, colourless, monoclinic prisms, $a : b : c = 1·0677 : 1 : 0·5533$; $\beta = 81° 24'$; observed faces $\infty\bar{P}\infty$, $\infty\grave{P}\infty$, 0P, ∞P, $\infty\grave{P}2$, and $+P$, and effloresces on exposure to the air; the *calcium* salt, with $3\frac{1}{2}$ mols. H_2O, is a white, microcrystalline powder, and the *calcium* salt with $6\frac{1}{2}$ mols. H_2O, crystallises in lustrous, large, colourless, monoclinic prisms, $a : b : c = 1·0899 : 1 : 0·6511$; $\beta = 89° 20'$; observed faces ∞P, $\infty\bar{P}2$, $\grave{P}\infty$, $-P$, $+\infty\bar{P}$, and $\infty\bar{P}\infty$, and effloresces slowly on exposure to the air; the *ethyl* salt, $C_{16}H_{14}(COOEt)_2$, crystallises from dilute alcohol in very slender, white, silky, matted needles, melts at 98°, and is very soluble in alcohol, ether, benzene, and acetic acid, sparingly soluble in light petroleum. γ-Truxillic anhydride can be prepared by heating γ-truxillic chloride with sodium γ-truxillate. W. P. W.

Derivatives of Nitrohydroxynaphthaquinone. By F. KEHRMANN and O. WEICHARDT (*J. pr. Chem.* [2], **40**, 179—187; compare Abstr., 1880, 940).—*Trihydroxy-β-naphthylamine hydrochloride*, $C_{10}H_4(OH)_3·NH_2,HCl$, is formed when sodonitrohydroxynaphthaquinone, in small portions at a time, is added to a solution of a little more than the theoretical quantity of stannous chloride in concentrated hydrochloric acid, and the mixture warmed with a little zinc. It separates from concentrated hydrochloric acid in large, monoclinic, colourless crystals, which turn greyish on exposure to light. The free *base*, $[(OH)_3 : NH_2 = 1 : 3 : 4 : 2]$, is obtained in greyish-white crystals when a solution of the hydrochloride is treated with sodium carbonate, but it is rapidly oxidised to amidohydroxynaphthaquinone. The *tetracetyl*-derivative, $C_{10}H_4(OAc)_3·NHAc$, prepared by boiling the hydrochloride with sodium acetate and acetic anhydride in presence of a little tin, crystallises from glacial acetic acid, melts at 145°, and is readily soluble in alcohol, chloroform, and concentrated acids, but insoluble in water. It dissolves unchanged in fuming nitric acid, and it is not acted on by a cold glacial acetic acid solution of chromic acid.

Acetamidohydroxynaphthaquinone, $OH·C_{10}H_4O_2·NHAc$, is formed when the preceding compound is treated for a long time with cold, concentrated potash in presence of air, or when amidohydroxynaphthaquinone is boiled with acetic anhydride. It crystallises from glacial acetic acid in yellow, indented needles, melts at 219—220°, and shows great resemblance to chlorhydroxynaphthaquinone. It is readily soluble in alcohol, glacial acetic acid, ether, chloroform, benzene, and carbon bisulphide, but insoluble in water; it dissolves in caustic alkalis with a blood-red coloration, and on adding alcohol the salts are precipitated in red crystals. When boiled for a long time with concentrated potash, it is decomposed, the solution becomes dark blue, and the potassium salt of amidohydroxynaphthaquinone separates on cooling in bluish-black needles. The *oxime*, $C_{12}H_{10}O_4N_2$, prepared by treating the quinone with hydroxylamine in alkaline solution, crystallises from glacial acetic acid and xylene in golden needles, decomposes at 190—200°, is sparingly soluble in alcohol, ether, benzene, and carbon bisulphide, and insoluble in water.

Amidohydroxynaphthaquinoneoxime, $C_{10}H_8O_3N_2$, prepared from amidohydroxynaphthaquinone in like manner, is a greenish-yellow, flocculent compound almost insoluble in the usual reagents, but soluble in alcoholic hydrochloric and acetic acids. It dissolves in alkalis with a violet coloration, which changes to blood-red on adding excess of alkali.

Diamidonaphtharesorcinol hydrochloride, $C_{10}H_4(OH)_2(NH_2)_2,2HCl$, is formed when the preceding compound is gradually added to a cold dilute hydrochloric acid solution of stannous chloride, and is precipitated in long, colourless needles on the addition of fuming hydrochloric acid. It oxidises and turns red on exposure to the air, either in the dry state or in solution. The alkaline solution rapidly oxidises, and becomes carmine-red; if the red solution is boiled for a short time ammonia is evolved, the solution turns black, and, on adding hydrochloric acid, amidohydroxynapthaquinone is precipitated. If the red alkaline solution is treated directly with acids, the colour darkens, and after a few minutes amidohydroxyquinone is precipitated. F. S. K.

Hydronaphthabenzylamines. By E. BAMBERGER and H. HELWIG (*Ber.*, **22**, 1912—1917; compare Abstr., 1887, 719, 840).—*Phenyl tetrahydro-β-naphthabenzylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot C_{10}H_{11}$, prepared by treating tetrahydronaphthabenzylamine with phenyl cyanate in benzene solution, crystallises from alcohol in slender, colourless needles, melts at 141°, and is readily soluble in acetone, alcohol, and chloroform, but almost insoluble in water. The corresponding *thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot C_{10}H_{11}$, crystallises from alcohol in colourless rosettes, melts at 139·5—140°, and is readily soluble in most ordinary solvents.

Tetrahydro-β-naphthabenzylcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot C_{10}H_{11}$, separates in colourless plates when a neutral solution of tetrahydronaphthabenzylamine hydrochloride is evaporated with potassium cyanate; it crystallises from hot alcohol in small plates, melts at 135—135·5°, and is soluble in alcohol, benzene, and ether.

Di-tetrahydro-β-naphthabenzylcarbamide, $CO(NH\cdot CH_2\cdot C_{10}H_{11})_2$, prepared by treating an acid solution of the base in like manner, crystallises from hot water in small plates melting at 225·5—226°.

Tetrahydro-β-naphthabenzylamine tetrahydro-β-naphthabenzyldithiocarbamate, $C_{10}H_{11}\cdot CH_2\cdot NH\cdot CS\cdot S\cdot NH_3\cdot CH_2\cdot C_{10}H_{11}$, is formed when the base is treated with carbon bisulphide in cold ethereal solution; it crystallises from alcohol in needles, melts at 128° with decomposition, and is sparingly soluble in water.

Di-tetrahydro-β-naphthabenzylthiocarbamide, $CS(NH·CH_2·C_{10}H_{11})_2$, obtained by boiling an alcoholic solution of the preceding compound, crystallises in nacreous plates, melts at 142·5—143°, and is readily soluble in chloroform, alcohol, and benzene, but more sparingly in ether, and insoluble in water.

Acetyltetrahydro-β-naphthabenzylamine, $C_{10}H_{11}·CH_2·NHAc$, crystallises from alcohol in long needles, melts at 64—65°, and is readily soluble in benzene, acetone, chloroform, alcohol, hot water, and light petroleum; it is not acted on by bromine in chloroform solution.

When tetrahydro-β-naphthabenzylamine hydrochloride is oxidised with 3 per cent. potassium permanganate in cold alkaline solution, phthalic acid and orthohydrocarboxycinnamic acid are formed.

Phenyltetrahydro-α-naphthabenzylcarbamide crystallises in colourless needles, melts at 126·5°, and is readily soluble in ether and warm alcohol.

Acetyltetrahydro-α-naphthabenzylamine crystallises in nacreous plates, and melts at about 88·5°.

When tetrahydro-α-naphthabenzylamine is oxidised with potassium permanganate, oxalic acid and phthalic acid are formed.

F. S. K.

α- and β-Naphthylglycines and their Derivatives. By O. Jolles (*Ber.*, **22**, 2371—2374).—Lippmann has shown that nitrosophenylglycine on reduction yields phenylhydrazidoacetic acid. The author is now extending this reaction to the naphthyl-series.

α-Naphthylglycine (Bischoff and Nastvogel, this vol., p. 1015) was prepared by heating α-naphthylamine with an aqueous solution of chloracetic acid. It forms a crystalline *platinochloride*, and its *silver salt* crystallises in silvery scales, but in aqueous solution decomposes on heating with formation of a metallic mirror. *α-Nitrosonaphthylglycine*, formed by acting on the ammonium salt with nitrous acid, is very unstable.

When β-naphthylamine is heated with aqueous chloracetic acid, *β-naphthylglycine-naphthylamine*, $C_{10}H_7·NH·CH_2·COOH,NH_2·C_{10}H_7$, is formed, and crystallises in yellow needles melting at 114—115°. When boiled with hydrochloric acid, this breaks up into naphthylamine and *β-naphthylglycine*. The latter forms microscopic crystals soluble in water, alcohol, ether, and glacial acetic acid, and melts at 134—135°. *β-Nitrosonaphthylglycine* is more stable than the corresponding α-compound; it crystallises from alcohol in reddish scales, and decomposes at 125—126°. L. T. T.

Condensation-derivatives of α-Naphthaldehyde. By E. Brandis (*Ber.*, **22**, 2148—2158).—α-Naphthaldehyde does not yield a crystallisable compound when treated with ammonia under the conditions employed in the preparation of hydrobenzamide from benzaldehyde; condensation with primary aromatic amines, however, gives better results. *α-Naphthabenzylidenaniline*, $C_{10}H_7·CH{:}NPh$, crystallises from alcohol in pale yellow needles, and melts at 71°; *α-naphthabenzylidenorthotoluidine*, $C_{10}H_7·CH{:}N·C_6H_4Me$, crystallises from alcohol in stellate groups of scales, and melts at 59°; *α-naphthabenzylideneparatoluidine* crystallises in long, yellow needles, and melts at 93°; *α-naphthabenzylidene-α-naphthylamine*, $C_{10}H_7\cdot CH:N\cdot C_{10}H_7$, crystallises in granular aggregates of prisms, melts at 117°, and is sparingly soluble in cold alcohol.

α-Naphthabenzaldoxime, $C_{10}H_7\cdot CH:N\cdot OH$, which crystallises from water in long, beautiful needles, melts at 98°, and is soluble in ether and alcohol, but only sparingly in hot water; it is reconverted into the aldehyde by boiling with hydrochloric acid.

The *nitrile* of *α-naphthaglycollic acid*, $C_{10}H_7\cdot CH(OH)\cdot CN$, is prepared by mixing α-naphthaldehyde (3 grams) and potassium cyanide (12 grams) with a small quantity of water, cooling in ice, and treating with concentrated hydrochloric acid (25 c.c.) added drop by drop. It is a thick, yellow oil, insoluble in water, but readily soluble in alcohol and ether. On hydrolysis with concentrated hydrochloric acid in the cold, it yields *α-naphthaglycollic acid*, $C_{10}H_7\cdot CH(OH)\cdot COOH$, which crystallises in rosettes of colourless needles, melts at 80—81°, and is soluble in water, readily soluble in ether and alcohol. The *barium* salt is microcrystalline, and is sparingly soluble in hot water.

α-Naphthacinnamic acid, $C_{10}H_7\cdot CH:CH\cdot COOH$, obtained from the aldehyde by Perkin's reaction, crystallises from alcohol in arborescent groups of needles, melts at 211—212°, and is very sparingly soluble in water, 1 part requiring 7,000 parts of hot water for its solution. The *calcium* salt crystallises in colourless, lustrous scales, and the *barium* salt forms tufts of needles. A second acid, which has not yet been obtained pure, is also formed in the reaction; it melts at 155—165°, yields α-naphthoic acid on oxidation with potassium permanganate, and is possibly an isomeric α-naphthacinnamic acid. *α-Naphthylpropionic acid*, $C_{10}H_7\cdot CH_2\cdot CH_2\cdot COOH$, formed by the reduction of the cinnamic acid with sodium amalgam, crystallises from alcohol in colourless needles, melts at 148°, and is somewhat sparingly soluble in hot water. *Dibrom-α-naphthahydrocinnamic acid*, $C_{10}H_7\cdot CHBr\cdot CHBr\cdot COOH$, prepared by brominating the cinnamic acid in chloroform solution, crystallises from chloroform in colourless scales, melts at 189°, and on reduction with zinc-dust and acetic acid is reconverted into α-naphthacinnamic acid. *α-Naphthyl-β-bromopropionic acid*, $C_{10}H_7\cdot CHBr\cdot CH_2\cdot COOH$, obtained by heating the cinnamic acid with 10 times its weight of hydrobromic acid (saturated at 0°) for 2½—3 hours at 100°, crystallises from chloroform in colourless needles, melts at 216°, and when suspended in water, and treated in the cold with an aqueous solution of sodium carbonate, is converted into *α-naphthacinnamene*, $C_{10}H_7\cdot CH:CH_2$. This is an oil with an aromatic odour resembling that of styrene, and yields on bromination in chloroform solution *α-naphthacinnamene dibromide*, $C_{10}H_7\cdot CHBr\cdot CH_2Br$, which crystallises in colourless tables, melts at 168°, and is very sparingly soluble in alcohol. W. P. W.

Decomposition of Sulphonic Acids in Presence of Phosphoric Acid. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, **109**, 95—99).—The decomposition of sulphonic acids by heating them with sulphuric acid and passing steam into the mixture is complicated by the formation of disulphonic acids and by other secondary reactions, and the yield of hydrocarbon is too low. Assuming that the sulphuric acid serves only as a medium which will contain a quantity of water sufficient for the decomposition, and the temperature of which can readily be regulated, the authors have substituted phosphoric acid for it with very satisfactory results. The sodium or potassium salt of the sulphonic acid is mixed with a considerable excess of phosphoric acid solution of 60° B. This liquid boils at 130°, and all the sulphuric acid which is liberated forms an acid sulphate of sodium or potassium; if necessary enough alkali may be added to form a normal sulphate. The operation is conducted in a glass retort, and the current of steam and the temperature are easily regulated. If necessary, the products at different stages of decomposition may be collected separately.

21 grams of tetrahydronaphthalene-monosulphonic acid (obtained by the action of sulphuric acid at 100° on that fraction of the products of the action of aluminium chloride on naphthalene which boils at 200°) gave 48·7 per cent. of tetrahydronaphthalene, instead of 53·4 per cent., and the amount of acid liberated was identical with the calculated quantity.

Experiments with benzene, metaxylene, and naphthalene and its derivatives indicate that the facility with which the monosulphonic acids decompose in this manner is in proportion to the ease with which they are formed. In like manner the monosulphonic acids are more easily decomposed than the disulphonic acids, many of the latter showing remarkable stability. Benzenedisulphonic acid is not decomposed below 280°, and the decomposition is not quite complete at 330°, because some of the acid distils over unchanged with the products of decomposition.

This method of separation of hydrocarbons may be applied to cases which have hitherto presented great difficulty, such as the separation of the naphthalene hydrides obtained by the action of aluminium chloride on naphthalene. It is found that the hydrocarbons which are converted into sulphonic acids are tetrahydronaphthalene and a small quantity of naphthalene, whilst the portion not attacked by the sulphuric acid consists of higher hydrides, especially the decahydride.

The naphthalene is the most readily converted into the sulphonic acid, and, in accordance with the rule already stated, naphthalene is found in the first portion of the products of decomposition by water in presence of phosphoric acid. C. H. B.

Oximes of Phenanthraquinone. By K. Auwers and V. Meyer (*Ber.*, **22**, 1985—1995; compare this vol., p. 609, and Beckmann, this vol., p. 980).—Attempts to prepare an isomeride of phenanthraquinoneoxime by treating the diketone with hydroxylamine under various conditions were unsuccessful, the only product in all cases being the monoxime (m. p. 158°) described by Goldschmidt (Abstr., 1884, 62).

When phenanthraquinone is treated with hydroxylamine in presence of alkali, the mixture at once turns green, and on warming for a few seconds a violent evolution of gas takes place; only small quantities of the monoxime are obtained, but considerable quantities of resinous products are formed. The result is the same, but the reaction is less energetic if excess of alkali is employed in the cold; when sodium carbonate is used, however, the yield of the monoxime is good.

Attempts to convert the monoxime into an isomeric compound by heating it with alcohol, or by treating it with a saturated acetic anhydride and glacial acetic acid solution of hydrogen chloride at various temperatures, were unsuccessful.

Phenanthraquinonedioxime, $C_{14}H_{10}N_2O_2$, can be prepared by digesting an alcoholic solution of phenanthraquinone (1 mol.) for 30 hours with hydroxylamine hydrochloride (4 mols.). It crystallises from alcohol or glacial acetic acid in microscopic, yellow prisms, melts at about 202° with previous decomposition, is insoluble in water, and only sparingly soluble in chloroform, benzene, alcohol, ether, and glacial acetic acid, but moderately easily in carbon bisulphide. It dissolves in concentrated sulphuric acid with a blood-red coloration, and in hot soda, yielding a yellow solution, from which the sparingly soluble *sodium*-derivative separates, on cooling, in nacreous plates. The *potassium*-derivative is readily soluble.

Attempts to prepare an isomeric dioxime by treating the diketone with hydroxylamine under various conditions were unsuccessful; when the dioxime is heated at 150° with alcohol, it is converted into the anhydride (m. p. 182—183°).

Diacetylphenanthraquinonedioxime, $C_{18}H_{14}N_2O_4$, is formed when the dioxime is dissolved in glacial acetic acid and acetic anhydride, and the solution saturated with hydrogen chloride in the cold. It separates from hot alcohol in microscopic, well-defined crystals, melts at 184°, is readily soluble in chloroform and benzene, and moderately so in carbon bisulphide, but only sparingly in alcohol, glacial acetic acid, ether, and light petroleum, and insoluble in water. When treated with cold dilute potash, it is slowly reconverted into the dioxime melting at 202°.

The above results show that phenanthraquinone only yields one monoxime and one dioxime under conditions which in the case of benzil lead to the formation of isomeric benziloximes, and, moreover, chemical agents which convert the benziloximes into isomeric compounds have no like action on the oximes of phenanthraquinone. It is probable, therefore, that structurally identical and stereochemically isomeric oximes of phenanthraquinone are incapable of existence, a conclusion which, if proved to be true, would be evidence in favour of the authors' views on the isomerism of the benziloximes (compare Auwers and Meyer, p. 611). F. S. K.

Terpin Hydrate. By G. VULPIUS (*Chem. Centr.*, 1889, i, 789, from *Pharm. Centralhalle*, **30**, 289—290).—The author attributes the inconsistencies in the recorded melting point and solubility of terpin hydrate as given by various writers, to the fact that the determinations have been made under different conditions. The melting point has been determined by some in the specimen either after drying in a desiccator or at a high temperature, by which means one of the three molecules of water is eliminated, and the substance melts at 102°, whereas, if the determination be carried out quickly under the least possible contact with the air, the substance melts at 116°. In like manner with regard to the solubility, this varies according to whether the solution be made by agitating the finely-powdered hydrate with the solvent in the cold, or whether it be dissolved with the aid of heat. In the latter case, terpin hydrate forms supersaturated solutions. In the former case it dissolves in 250 parts of water, 10 parts of alcohol, 100 parts of ether, and 200 parts of chloroform; whilst in the latter case it only requires 32 parts of boiling water, and only 2 parts of hot alcohol for solution. J. W. L.

Oxidation by Nitrosocamphor in presence of Light. By P. Cazeneuve (*Compt. rend.*, **109**, 185—187).—When dry nitrosocamphor is exposed to light, nitrogen oxides are evolved; in presence of water, nitrogen is given off, and substances in contact with the nitrosocamphor are oxidised.

In presence of water alone, the decomposition is very slow; nitrogen is liberated, but no carbonic anhydride, nitric oxide, nor other oxide of nitrogen is given off. Even after long exposure, the residue contains 5 per cent. of nitrogen, has a greenish tint, and dissolves readily in cold alcohol of 85°. It probably has a complicated composition, but it no longer gives Liebermann's reaction with phenol and sulphuric acid, so that the nitroso-group must have disappeared. Acetic chloride has no action, and hence hydroxyl-groups are absent, but the partial solubility of the substance in alkalis indicates that some acid has been formed.

When excess of alcohol is mixed with nitroso-camphor and exposed to light, there is rapid evolution of nitrogen and a proportional production of aldehyde mixed with a small quantity of glycollic acid, but no acetic acid is formed. A 5 per cent. aqueous solution of mannitol is converted into mannitose and an acid which seems to be mannitic acid. Glycerol in 30 per cent. aqueous solution is converted into glyceraldehydes. With excess of nitroso-camphor, oxidation would probably proceed further; oxalic and formic acids in 1 per cent. solution are oxidised to carbonic anhydride.

The author suggests that many changes in the vegetable kingdom, such as the formation of chlorophyll and other colouring matters, may be due to oxidation produced by certain substances under the influence of light. Nitrosocamphor and naphthylamine hydrochloride yield a substance which is first violet-red, and then orange-red, and is known to be formed in the vegetable kingdom under the influence of light. C. H. B.

Monochlorocamphor formed by the Action of Hypochlorous Acid. By P. Cazeneuve (*Compt. rend.*, **109**, 229—231).—If powdered camphor is agitated with concentrated hypochlorous acid, it rapidly liquefies and then suddenly solidifies with considerable rise of temperature. The product is washed with water, dissolved in alcohol of 93°, mixed with potassium hydroxide in slight excess, and precipitated by water. It is then purified by crystallisation from alcohol, and finally from chloroform.

The aqueous alkaline liquid contains a small quantity of a liquid which seems to be an additive product; it has an odour of camphor, contains chlorine, dissolves in potassium hydroxide, gives a slight red coloration with ferric chloride, and is attacked by acetic chloride.

The monochlorocamphor obtained in this way resembles terebenthene hydrochloride, and is a soft, crystalline substance, which melts at 124—125° (not 95°, as stated by Wheeler), and boils at 220° with slight decomposition. It dissolves in alcohol, ether, and chloroform, and its rotatory power is $[\alpha]_D = +40°$. It is only very slightly and slowly decomposed by boiling water, even in presence of lead oxide; it is slowly decomposed by alcoholic potash, with formation of camphor and unstable acid products. When boiled with fuming nitric acid, it yields some camphoric acid and a nitrochlorocamphor, which forms metallic derivatives with zinc and iron. If heated with aqueous ammonia at 150° for 24 hours, it yields a readily oxidisable base, which has a very powerful odour, and is precipitated by all the group reagents for the alkaloïds. The base and the hydrochloride and picrate are very soluble and non-crystallisable, but the platinochloride seems to crystallise.

When heated with strong sulphuric acid, the chlorocamphor yields hydrochloric acid and phenolic compounds containing sulphur; when distilled with powdered zinc, it yields a considerable quantity of cyanogen.

The stability of the compound indicates that substitution has not taken place in the methyl- or propyl-chains, and that it has not a constitution analogous to benzyl chloride. On the other hand, its stability is not great enough to lead to the conclusion that substitution has taken place in a CH-group in the nucleus. It is most probable that, as in normal monochlorocamphor, substitution has taken place in a CH_2-group in the nucleus. C. H. B.

Isomeride of Monobromocamphor. By P. Cazeneuve (*Compt. rend.*, **109**, 439—441).—Hypobromous acid is prepared by the action of bromine on mercuric oxide suspended in water cooled at 0°, and powdered camphor is agitated briskly with the solution. It forms a reddish-orange liquid, which is washed with cold water, dissolved in alcohol of 93°, agitated with a slight excess of potassium hydroxide to remove bromine, precipitated by the addition of water, washed, dried, and finally crystallised from alcohol of 85°, and from chloroform.

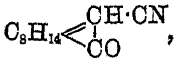
The monobromocamphor thus obtained forms ill-defined crystals, which melt at 144—145°, whilst ordinary monobromocamphor melts at 76°. It is insoluble in water, but readily dissolves in alcohol, benzene, ether, and chloroform. A 5·5 per cent. solution in alcohol of 93° has a rotatory power of $[\alpha]_D = +40°$, which is identical with that of the monochlorcamphor obtained by the action of hypochlorous acid (preceding abstract). With water and dilute acids at high temperatures, with ammonia, and in all reactions (*loc. cit.*) the two derivatives behave in a precisely similar manner. They are therefore doubtless similar in constitution, and the bromine has displaced hydrogen in a CH_2 group of the nucleus.

The monochloro- and monobromo-derivatives obtained respectively by the direct action of bromine, or the action of chlorine in presence of alcohol, contain the halogen in the ortho-relation to the carboxyl. It is probable that the isomerides contain the halogen in the para-relation, but they may also be regarded as ethereal salts of a secondary alcohol with the $CH\cdot OH$ group in the nucleus. The latter view is supported by the liberation of hydrochloric or hydrobromic acid by the action of water or dilute sulphuric acid at 150°, and by the production of amines on treatment with ammonia. C. H. B.

Camphor-derivatives. By A. HALLER (*Compt. rend.*, **109**, 68—71 and 112—114).—Cyanocamphor remains unaltered when heated with alcohol alone, but in presence of a small quantity of sodium a reaction takes place, and if the product is concentrated and the crystals which form are washed with a solution of potassium hydroxide and recrystallised from ether, the compound $CN\cdot C_{10}H_{16}O_2Et$ is obtained in rhombic crystals which melt at 57—58° and are insoluble in water and in alkalies, and only slightly soluble in light petroleum, but dissolve in ether and in alcohol; molecular rotatory power in alcoholic solution $[\alpha]_D = +57° 70'$. This compound gives no reaction with ferric chloride, and does not reduce Barreswill's solution nor silver nitrate. The formation of this compound takes place readily under atmospheric pressure, but it is better to conduct the operation in sealed tubes at 100°. The same product is obtained by the action of sodium amalgam on an alcoholic solution of cyanocamphor.

Methyl alcohol under similar conditions yields the compound $CN\cdot C_{10}H_{16}O_2Me$, which forms crystals melting at 76—77°. The corresponding propyl-derivative is an oily liquid, which does not solidify at −20°, and dissolves in most solvents, except water and alkalis.

If cyanocamphor is assumed to have the constitution



$$C_8H_{14}{<}\begin{matrix}CH\cdot CN\\ |\\ CO\end{matrix},$$

the question arises whether the cyanogen-group has the same influence on the CO-group as the CCl_3-group has on the COH-group in chloral. The formula, $\genfrac{}{}{0pt}{}{RO}{HO}{>}C{<}\begin{matrix}CHCN\\ |\\ C_8H_{14}\end{matrix}$, is, however, inadmissible, because the alkyl-derivatives yield neither acetyl- nor benzoyl-derivatives when treated with the corresponding chlorides. It may also be assumed that cyanocamphor has the constitution, $C_8H_{14}{<}\begin{matrix}C\cdot CN\\ \|\\ C\cdot OH\end{matrix}$. The formula, $\genfrac{}{}{0pt}{}{RO}{CN}{>}C{<}\begin{matrix}CH\cdot OH\\ |\\ C_8H_{14}\end{matrix}$, is, however, inadmissible, because the alkyl-derivatives yield no ethereal salts. Still, assuming that the double bond is unloosed, the constitution of the alkyl-derivatives may be $COOEt\cdot C_8H_{14}\cdot CH_2\cdot CN$, that is to say, they are ethereal salts of the acid $COOH \cdot C_8H_{14} \cdot CH_2 \cdot CN$, which is itself the nitrile of hydrocampho-carboxylic acid.

The author has previously shown that when cyanocamphor is treated with concentrated potash it yields hydrocamphocarboxylic acid. When this is heated with alcohol and hydrochloric acid, it yields a small proportion of a diethyl salt, with a molecular rotatory power of +45°, and a much larger proportion of the monethyl salt, a semi-crystalline solid, which melts at 44—45°.

When the ethyl-derivative obtained from a cyanocamphor is treated with concentrated hydrochloric acid, it yields ammonia, alcohol, and hydrocamphocarboxylic acid. Cyanocamphor under the same conditions yields camphocarboxylic acid. The ethyl-derivative also yields hydrocamphocarboxylic acid when treated with excess of potash. With an alcoholic solution of hydrogen chloride, it yields the diethyl salt of the acid, and if this ethereal salt is treated with alcoholic potash in molecular proportion, it yields the potassium salt of an acid, which melts at 77—78°, and is isomeric with the monethyl salt of hydrocamphocarboxylic acid. The same compound is obtained if the original ethyl-derivative is boiled with alcoholic potash in molecular proportion, until ammonia is no longer evolved.

These results confirm the supposition that the double bond is unloosed, the change being facilitated by the presence of the negative cyanogen-group. The two carboxyl-groups in the product do not yield alkyl salts with the same readiness, and when these salts are formed they differ considerably in stability. It follows that the energy of the acid function of the group CO·OH depends on the nature of the nucleus or radicle with which it is combined. CH. B.

Influence of Solvents on the Rotatory Power of Isocamphols.

By A. HALLER (*Compt. rend.*, **109**, 187—1)).—The author distinguishes the stable camphols as α-camphols and the unstable as isocamphols or β-camphols.

Lævogyrate isocamphol prepared by Montgolfier's method resembles its isomeride ordinary or α-camphol, but is more soluble in alcohol, benzene, toluene, and petroleum. In capillary tubes it volatilises without melting, but in sealed tubes it melts at 212°. From light petroleum it crystallises in fern-like leaflets and not in hexagonal tables like its isomeride.

α-camphol has the same rotatory-power (+ 38·52) in alcohol, toluene, or petroleum, but the rotatory power of isocamphol varies with the solvent. In alcohol it is —33·11, in petroleum -26·62, and in toluene —20·99. A mixture of equivalent quantities of dextrogyrate α-camphol and lævogyrate isocamphol is inactive in alcoholic solution, but in petroleum it has a rotatory power of +3 and in toluene of +7·01. It will be observed that these differences are lower than those observed with the isocamphol alone.

A mixture of dextrogyrate isocamphol with a slight excess of lævogyrate α-camphol had a rotatory power of —1·30 in alcohol, —5·19 in petroleum, and —6·49 in toluene.

It is evident that the influence of solvents on the rotatory power may vary with different isomerides, and that, in this particular instance the differences may be utilised to distinguish between the α-camphols and the isocamphols. C. H. B.

Molecular Weight of Caoutchouc and other Colloid Substances. By J. H. GLADSTONE and W. HIBBERT (*Phil. Mag.* [5], **28**, 38—42).—The authors have determined the molecular weight of caoutchouc by Raoult's method. The caoutchouc was prepared from Penang and Para rubber, and was purified by three different methods. The experiments were made on solutions in benzene of 5·25° freezing-point. Only one of the three samples gave measurable results (mol. weight 6504), and as it had been separated from its ethereal solution by evaporation in hydrogen, the authors consider that a lowering of the molecular weight had taken place. The accuracy of Raoult's method for substances of this nature had been previously proved by experiments with substances of the same ultimate constitution (oil of turpentine, oil of lemon, cedrene, caoutchene, &c.) whose molecular weight was known. Extremely concordant results were obtained. The high molecular weight obtained for caoutchouc, the total absence of any tendency to crystallise, its decomposition when distilled, its easy alterability by the action of heat, and the extreme slowness with which it dissolves, render it probable that caoutchouc belongs to the class of colloids. For this reason, experiments were made with gum arabic, caramel, and albumin in aqueous solution. Very high molecular weights (about 2000) were obtained; a result which agrees with the experiments of Brown and Morris (Trans., 1888, 610). Experiments were also made with solutions of the colloidal hydrates of iron and aluminium; the molecular weights obtained were very high, especially if due allowance is made for the small amount of chloride which is unavoidably present. All the authors' experiments, therefore, confirm the belief that the colloid molecule contains a very large number of atoms. H. K. T.

Colouring Matter of Purpura lapillus. By A. LETELLIER (*Compt. rend.*, **109**, 82—85).—*Purpura lapillus* is very abundant on the coast of Brittany, and is probably the source from which the ancient Britons obtained their purple dye. The colouring matter is furnished by a yellowish-white fascia which extends along the rectum, and is only developed on exposure to light. Three substances seem to be concerned in the production of the purple. One is yellow and is non-photogenic, while the other two are green and rapidly become blue or carmine when exposed to light. The yellow substance crystallises in oblique prisms or in very thin plates, which resemble crystals of uric acid but are triclinic. It is soluble in potassium hydroxide and is precipitated unchanged on the addition of a dilute acid.

One of the two photogenic substances is apple-green in colour, and the crystals, which are monoclinic, resemble magenta in general appearance, but rapidly become opaque and dark blue when exposed to light. It dissolves with difficulty in water but is readily soluble in chloroform and especially in light petroleum. The other forms dull-green rhombic crystals, which are relatively somewhat soluble in water and become violet or carmine-red on exposure to light.

In order to obtain these compounds the fasciæ of hundreds of *Purpura* are dried over sulphuric acid in a vacuum, powdered, and extracted with ether. The ethereal solution is evaporated and the residue treated with potash in order to remove fats and the yellow substance. The latter is precipitated by acidifying the solution. That portion of the residue which is insoluble in potash is treated with chloroform, which dissolves the dull-green compound more readily than the other, or with light petroleum, which first dissolves the apple-green substance. All these operations must be conducted in the dark.

When the purple colouring matter has once been formed, it is a dark impalpable powder quite insoluble in all ordinary solvents. Nitric acid or chlorine water decomposes it; strong sulphuric acid converts it into an emerald-green substance which, on addition of water, forms a deep indigo-blue solution, but prolonged contact with the acid results in carbonisation.

When the powder is suspended in chloroform, the liquid transmits only the rays 720—613 and 535—490. If the purpurogenic substances are dissolved in chloroform and the solution is exposed to the prismatic spectrum of the electric arc, it is found that the green and the less refrangible part of the blue have no action, whilst the red and infra-red are very active and under these conditions produce a greater effect than the violet and ultra-violet. There is little doubt, however, that the colouring matter is a product of reduction. If the purpurogenic substances are mixed with hypochlorous acid, hydrogen peroxide, or potassium dichromate, they remain unaltered, but when treated with sodium amalgam a purple-red substance is formed. When the purple is oxidised, it becomes white, but on exposure to light it again becomes green and finally rose-coloured.

The purpurogenic substances are most abundant between October and April, the time during which reproduction takes place.

C. H. B.

Conversion of Pyrroline into Tetramethylenediamine. By G. Ciamician and C. U. Zanetti (*Ber.*, 22, 1968—1975).—Pyrrolinehydroxylamine (compare Ciamician and Dennstedt, Abstr., 1885, p. 246) is best prepared by boiling pyrroline (10 grams) for 17 hours with hydroxylamine hydrochloride (12 grams) and anhydrous sodium carbonate (8 grams) in 90 per cent. alcoholic solution (100 grams). The yield is 35 per cent. It melts at 173°, and molecular weight determinations by Raoult's method in glacial acetic acid solution gave results in accordance with those required by the molecular formula $C_4H_8N_2O_2$. When treated with sodium in boiling alcoholic solution, it is converted into tetramethylenediamine, melting at 27—28°, and identical in all respects, save in melting point, with the compound (m. p. 23—24°) described by Ladenburg (Abstr., 1886, 528). The benzoyl-derivative melts at 177—178°; Udránszky and Baumann (this vol., p. 33) give 175—176° as the melting point of this compound. The constitution of the compound $C_4H_8N_2O_2$ is probably $OH{\cdot}N{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}N{\cdot}OH$ (succinaldoxime); it is soluble in alkalis, reacts with acetic anhydride, and when treated with nitrous acid nitrous oxide is evolved.

A compound, $C_{16}H_{18}N_4$, probably *succindihydrazone*, is formed when pyrrolinehydroxylamine (0·5 gram) is heated at 210° for a few minutes with phenylhydrazine (1 gram). It crystallises from boiling alcohol in almost colourless, silky plates, melts at 124—125°, and is decomposed at a higher temperature; it is readily soluble in alcohol, ether, and benzene, but insoluble in water. It turns reddish-yellow on exposure to light and air or when heated for a long time at 100°.

F. S. K.

2- and 3-Methylpyrroline. By M. DENNSTEDT and A. LEHNE (*Ber.*, **22**, 1918—1920; compare Abstr., 1886, 1043).—The 2- and 3-methylpyrrolines which are present in small quantities in the fraction of Dippel's oil, boiling at 140—153°, cannot be completely separated by the method previously described (*loc. cit.*), as only the 2-compound (b. p. 147—148°), which forms the larger proportion of the mixture, can be obtained in a pure state; the dimethylindole, prepared from the 3-methylpyrroline (this vol., p. 400), may, therefore, have only been obtained in an impure condition.

2-*Methylpyrryl cinnamyl ketone*, $C_4NH_3Me{\cdot}CO{\cdot}CH{:}CHPh$, prepared by boiling the acetyl-derivative of 2-methylpyrroline with benzaldehyde and very dilute potash, crystallises from alcohol in compact yellow needles melting at 193°. The corresponding 3-*compound*, prepared in like manner, crystallises from alcohol in small, light yellow plates and melts at 156—157°. F. S. K.

Dimethylpyrrolines. By M. DENNSTEDT (*Ber.*, **22**, 1920—1924).—2,4-*Dimethylpyrryl cinnamyl ketone*, $C_4NH_2Me_2{\cdot}CO{\cdot}CH{:}CHPh$, prepared from 5-acetyl-2,4-dimethylpyrroline and benzaldehyde, crystallises from alcohol in small, yellow plates melting at 188°. When 2,3-dimethylpyrroline is treated with hydrogen chloride in ethereal solution (compare this vol., p. 400), small quantities of a very unstable condensation-product are formed, from which, however, an indole-derivative cannot be obtained by treating it with sulphuric acid.

Tetramethylindole, $C_{12}H_{15}N$, is obtained when an aqueous solution of tetramethyldipyrroline hydrochloride (compare Dennstedt and Zimmermann, Abstr., 1887, 598) is mixed with dilute sulphuric acid and, after keeping for some days, the product is distilled with steam. It is a yellowish oil, boils at 285° with partial decomposition, and is soluble in concentrated hydrochloric acid, but is reprecipitated on adding water. When heated at 120° for 15 hours with methyl alcohol and methyl iodide, it yields a yellow oil which shows all the characteristic reactions of a dihydroquinoline. The *picrate*, prepared by treating the base with picric acid in benzene solution, crystallises in granite-red needles melting at about 100° with decomposition.

The conversion of the dimethylpyrroline (b. p. 165°) obtained from Dippel's oil into tetramethylindole seems to show the presence of 2,3-dimethylpyrroline in the original oil (compare following abstract).

F. S. K.

Dimethylpyrrolines in Dippel's Oil. By M. DENNSTEDT (*Ber.*, **22**, 1924—1929).—The presence of 2,3-dimethylpyrroline in Dippel's oil is rendered probable by the experiments already described (compare preceding abstract) and also from the behaviour of the oil with acetic anhydride.

If the fraction (b. p. 165°) obtained from coal-tar contains 2,3-dimethylpyrroline it should yield a *c*-acetyl-derivative; if on the other hand 2,5-dimethylpyrroline alone is present an *n*-acetyl-derivative only should be obtained, as was found to be the case by Weidel and Ciamician (Abstr., 1880, 403).

The compound (m. p. 83—85°) previously obtained by Zimmermann and Dennstedt (Abstr., 1886, 1043) from this fraction of the oil and which was thought by them to be a *c*-acetyldimethylpyrroline has now been found to be a *c*-acetylmethylpyrroline identical with the compound (m. p. 85—86°) prepared by Ciamician and Silber (Abstr., 1886, 719).

When the oil (b. p. 165°) is heated at 190° for 3 to 4 hours with acetic anhydride and sodium acetate, and the product distilled with steam, the 1-acetyl-derivative prepared by Weidel and Ciamician (*loc. cit.*) and a small quantity of a *c*-acetyl-derivative, boiling at 250—260°, are obtained. The latter could not be prepared in a pure condition, but it was identified by means of its silver derivative and by converting it into the pyrryl cinnamyl ketone. The *silver*-derivative, $C_8H_{10}NOAg$, is a colourless crystalline compound which darkens on exposure to light. *Dimethylpyrryl cinnamyl ketone*,

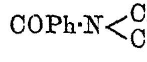
$$C_4NH_2Me_2\cdot CO\cdot CH{:}CHPh,$$

crystallises from boiling alcohol in plates or needles melting at 166°.

A pyrroline fraction boiling constantly at 154—156° was proved, by its behaviour with acetic anhydride, to consist of a mixture of 2-methylpyrroline (b. p. 147—148°) and a dimethylpyrroline (b. p. 165), the acetyl-derivative of which yields the dimethylpyrryl cinnamyl ketone melting at 166°.

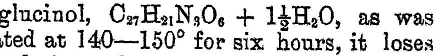
A pyrroline fraction boiling at 171—172° gave on analysis results agreeing fairly well with the composition of a trimethylpyrroline; when heated with acetic anhydride, it yielded an acetyl-derivative from which a yellowish crystalline compound, melting at 142° and isomeric with that prepared from isopropylpyrroline (Abstr., 1887, 598), was obtained. F. S. K.

Compounds obtained, together with Dibenzamidodihydroxytetrene by the Action of Sodium Ethoxide on Ethyl Hippurate. By L. Rügheimer (*Ber.*, 22, 1954—1965; compare this vol., p. 249).—The compound obtained, together with dibenzamidodihydroxytetrene, by the action of sodium ethoxide on ethyl hippurate is most probably *benzoyltrihydroxybenzamidopyrroline*,



$$\mathrm{COPh\cdot N}<\begin{array}{l}\mathrm{CH{:}C(OH)}\\ \mathrm{C(OH)_2}\text{——}\end{array}>\mathrm{CH\cdot NH\cdot COPh}$$

or



$$\mathrm{COPh\cdot N}<\begin{array}{l}\mathrm{CH_2C(OH)}\\ \mathrm{C(OH)_2}\text{——}\end{array}>\mathrm{CH\cdot NH\cdot COPh},$$

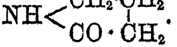
and not tribenzamidophloroglucinol, $C_{27}H_{21}N_3O_6 + 1\frac{1}{2}H_2O$, as was previously stated. When heated at 140—150° for six hours, it loses benzoic acid and is converted into dihydroxybenzamidopyrroline (m. p. 200·5°), identical with the compound obtained by treating dibenzamidodihydroxytetrene with hydrochloric acid in presence of methyl alcohol. When heated with a mixture of equal parts of sulphuric acid, glacial acetic acid, and water, it is decomposed into diamidoacetone, benzoic acid, and carbonic anhydride. The *barium* salt, $C_{18}H_{14}N_2O_5Ba$, is colourless and very hygroscopic. The lead salt previously described must have been impure and the composition assigned to it is incorrect.

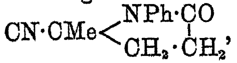
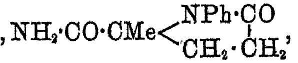
Diamidoacetone sulphate is very readily soluble in water; on adding alcohol to the aqueous solution, it first separates as an oil and then becomes crystalline. The platinochloride crystallises in various forms according to the conditions of the experiment.

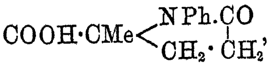
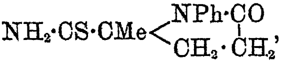
Dihydroxybenzamidopyrroline is sparingly soluble in hot water but readily in alcohol; with ferric chloride, the alcoholic solution gives a blue coloration which turns green on adding more of the iron salt. When heated with a mixture of equal parts of sulphuric acid, glacial acetic acid and water, it is decomposed into benzoic acid, carbonic anhydride, and diamidoacetone. The calcium, barium, lead, zinc, copper, and silver derivatives are readily soluble in water; a solution of the silver salt decomposes with separation of silver, even in the dark.

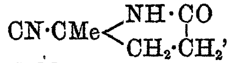
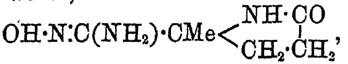
The compound $C_{36}H_{28}N_4O_6$ which is formed, but only in very small quantity, by the action of sodium ethoxide on ethyl hippurate, crystallises from glacial acetic acid in small, yellowish needles, and does not melt below 270°. It is only very sparingly soluble in hot glacial acetic acid and almost insoluble in hot alcohol, but it dissolves slowly in cold sodium carbonate and in cold baryta. When heated at 130° for two hours with a mixture of equal parts of sulphuric acid, glacial acetic acid, and water, it is almost completely decomposed, yielding benzoic acid and resinous products. The *barium* salt, $C_{36}H_{26}N_4O_6Ba$, is very sparingly soluble in water and crystallises in small, yellow needles. The calcium salt, $C_{36}H_{26}N_4O_6Ca$, is yellow and only sparingly soluble. In aqueous solutions of the barium salt, calcium chloride produces a yellow, copper acetate, a light green and silver nitrate, a light yellow precipitate which turns brownish-red even in the dark.

F. S. K.

Derivatives of Pyrrolidone. By O. KÜHLING (*Ber.*, 22 2364—2371).—When the hydroxynitrile of levulinic acid is treated with ammonia or an amine, the elements of water are separated and the amido-group substituted. The first product, however, is very unstable, condensation immediately taking place, with formation of a derivative of pyrrolidone,  $NH<\begin{matrix}CH_2\cdot CH_2\\ | \\ CO\cdot CH_2\end{matrix}$.

Using aniline in this way, *phenylmethylpyrrolidonecarbonitrile*,  $CN\cdot CMe<\begin{matrix}NPh\cdot CO\\ | \\ CH_2\cdot CH_2\end{matrix}$, is formed. It is a thick oil which could not be obtained in a crystalline form. When this is treated with cold sulphuric acid, the *amide*,  $NH_2\cdot CO\cdot CMe<\begin{matrix}NPh\cdot CO\\ | \\ CH_2\cdot CH_2\end{matrix}$, is produced, which is soluble in alcohol, benzene, and glacial acetic acid, sparingly so in water, crystallises in colourless needles, and melts at 127°. *Phenyl-*

methylpyrrolidonecarboxylic acid,  $COOH\cdot CMe<\begin{matrix}NPh.CO\\ CH_2\cdot CH_2\end{matrix}$, may be obtained from the amide or the nitrile. It yields hard prisms soluble in alcohol, sparingly so in water and insoluble in ether and melts at 183°. The *barium* and *silver* salts are crystalline. The *thiamide*,  $NH_2\cdot CS\cdot CMe<\begin{matrix}NPh\cdot CO\\ CH_2\cdot CH_2\end{matrix}$, is formed when the nitrile, suspended in water, is treated with ammonia and hydrogen sulphide. It crystallises in needles, melts at 193°, and is only sparingly soluble in water and alcohol. The *amidoxime* is obtained by acting on the nitrile with hydroxylamine, is crystalline, and melts with decomposition at 120°.

When ammonia is used in place of aniline, *methylpyrrolidonecarbonitrile*,  $CN\cdot CMe<\begin{matrix}NH\cdot CO\\ CH_2\cdot CH_2\end{matrix}$, is formed. It yields octahedral crystals, easily soluble in water and melting at 141°. It appears to undergo decompositions similar to the phenylated-derivative, but the author has not yet obtained the amide or acid in a pure state. The *thiamide* is sparingly soluble in water, and melts with decomposition at 220°. The amidoxime,  $OH\cdot N{:}C(NH_2)\cdot CMe<\begin{matrix}NH\cdot CO\\ CH_2\cdot CH_2\end{matrix}$, crystallises from boiling water in steel-blue needles, and melts at 156°.

L. T. T.

Preparation of Monobromo- and Dibromo-pyridine. By F. BLAU (*Monatsh.*, **10**, 372—374).—The method which the author describes gives about the same yield as that obtained by Ciamician and Silber (Abstr., 1885, 811), using Hofmann's mode of preparation. It, however, has the advantage of not requiring sealed tubes, the pyridine (100 grams), in the form of sulphate or hydrochloride, being heated in a retort, provided with an air-condenser, until dissociation occurs, when bromine-vapour (200 grams) is passed in. The whole operation takes from six to eight hours. G. T. M.

2,6-Diphenylpyridine. By O. DÖBNER and P. KUNTZE (*Annalen*, **252**, 349—350).—The authors find that the 2,6-diphenylpyridine, which they obtained from 2,6-diphenylpyridinecarboxylic acid (prepared by the oxidation of α-phenyl-α-napthacinchonic acid (this vol., p. 411), is identical with the diphenylpyridine from diphenacylacetic acid, described by Paal and Strasser (Abstr., 1888, 63).

W. C. W.

Distillation of the Salts of Pyridinecarboxylic Acid. By F. BLAU (*Monatsh.*, **10**, 375—388; compare Abstr., 1888, 728).—On dry distillation, copper picolinate yields copper, carbon dioxide, and almost equal parts of pyridine and *α-dipyridyl*, $C_{10}H_8N_2$. The last-named compound melts at 69·5°, boils at 272·5°, and can be distilled unchanged. It has a pleasant, strongly aromatic odour; is a feeble base, the aqueous solution scarcely affecting red litmus; is readily dissolved by all ordinary solvents, except water, and forms readily soluble salts with the mineral acids. On adding ferrous sulphate to a dilute solution of the base, a very characteristic red coloration is obtained. On oxidising the base (3 grams) dissolved in water containing sulphuric acid (2 grams) with a 3 per cent. solution of permanganate (20 grams), the solution being kept nearly neutral by occasionally adding sulphuric acid, picolinic acid is again formed.

Tin and hydrochloric acid are almost without reducing action on α-dypyridyl, but zinc or cadmium and hydrochloric acid reduce the base with the formation of a strongly alkaline oil, which, from the analysis of a platinochloride obtained from it, appears to be hexahydrodipyridyl. On reduction with sodium in an amyl alcoholic solution, just twice as many atoms of hydrogen are taken up with formation of *α-dipiperidyl*, $C_{10}H_{20}N_2$. This is a very powerful base which precipitates many metals from their solutions as hydroxides, and is exceedingly hygroscopic, dehydrating even commercial potash. It melts at 259° (corr.), and when 8 centigrams of it, as hydrochloride, was injected into a rabbit, no toxicological effect was observed. α-Dipiperidyl is a secondary base and consequently unites readily with carbon bisulphide, forming a compound sparingly soluble in alcohol, and melting at 92—93°. With nitrous acid, dipiperidyl yields a nitroso-compound, which crystallises from alcohol and melts at 159°. G. T. M.

Truxillopiperidides and Truxillopiperididic Acids. By B. Herstein (*Ber.*, **22**, 2261—2265).—*Piperidine-γ-truxillopiperididate*, $C_5NH_{10}{\cdot}CO{\cdot}C_{16}H_{14}{\cdot}COOH,C_5NH_{11} + 3H_2O$, is prepared by the action of γ-truxillic anhydride (1 mol.) on piperidine (2 mols.). It crystallises from alcohol in colourless tables, melts at 218°, and is sparingly soluble in cold water. On treatment in aqueous solution with hydrochloric acid, it yields *γ-truxillopiperididic acid*, $C_5NH_{10}{\cdot}CO{\cdot}C_{16}H_{14}{\cdot}COOH$, which crystallises in lustrous scales, melts at 261°, is sparingly soluble in cold but readily in hot alcohol, insoluble in water, benzene, and ether; when heated with hydrochloric acid (sp. gr. = 1·125) at 175°, it is converted into α- and not into γ-truxillic acid, the liberated γ-acid undergoing isomeric change in the presence of the hydrochloric acid (compare Liebermann, this vol., p. 1194). The *methyl* salt, $C_{23}H_{24}NO_3Me$, crystallises in colourless needles or scales, melts at 201°, and is insoluble in alkalis, but soluble in warm, dilute hydrochloric acid. *γ-truxillopiperidide*, $C_{16}H_{14}(CO{\cdot}C_5NH_{10})_2$, formed by the action of γ-truxillic chloride (1 mol.) on piperidine (2 mols.), crystallises from alcohol in silky, white needles, melts at 248°, and yields α-truxillic acid and piperidine hydrochloride when heated at 175° with dilute hydrochloric acid.

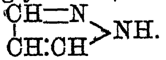
α-Truxillopiperididic acid, $C_{23}H_{25}NO_3$, forms a crystalline powder, melts at 250°, is moderately soluble in alcohol, and resembles the γ-acid in its properties. The *methyl* salt crystallises from ether in needles, and melts at 151°. *α-Truxillopiperidide*, $C_{28}H_{34}N_2O_2$, is a white crystalline powder, which melts at 259°, and yields α-truxillic acid and piperidine hydrochloride on hydrolysis with hydrochloric acid at 250°.

β-Truxillopiperididic acid crystallises in needles, melts at 224°, is sparingly soluble in cold alcohol, and decomposes more readily than its isomerides when boiled with dilute acids or alkalis. *β-Truxillopiperidide* crystallises in prisms, melts at 180°, is very readily soluble in alcohol, and undergoes hydrolysis into β-truxillic acid and diperidine hydrochloride when heated with acidified water at 120°.

Cinnamylpiperidide, $C_8H_7 \cdot CO \cdot NC_5H_{10}$, crystallises in stellate groups of white needles, melts at 122°, and is soluble in alcohol, insoluble in water and alkalis. Hydrochloric acid dissolves it readily, and an unstable *hydrochloride* can be obtained; this crystallises from alcoholic hydrogen chloride in prisms, and effloresces on exposure to the air with loss of hydrogen chloride. W .P. W.

Quinoline. By H. ALT (*Annalen*, **252**, 318—330).—Metabromorthacetotoluide is most conveniently prepared by the action of bromine on orthacetoluide in presence of acetic acid. The purified product melts at 156—157°. It is decomposed by boiling with strong hydrochloric acid in presence of alcohol, yielding metabromorthotoluidine (m. p. 59·5°). The sulphate crystallises with 2 mols. H_2O.

Parabromorthotoluquinoline is prepared by heating 10 grams of metabromorthotoluidine, 6 grams of orthonitrophenol, 25 grams of glycerol, and 20 grams of sulphuric acid at 160—180° for 6 hours. The mixture is diluted with water, and the nitrophenol distilled off in a current of steam; the base is liberated by the addition of an alkali, and is distilled. It melts at 59°, boils at 289—290°, and is freely soluble in benzene, alcohol, ether, carbon bisulphide, and chloroform. The *ferrocyanide*, *picrate*, and *platinochloride* are sparingly soluble crystalline salts. In order to prepare the tetrahydro-derivative, bromotoluquinoline (3 or 4 grams) is dissolved in warm, strong, hydrochloric acid, granulated tin is added, and the mixture heated at 100° for 4 hours; on cooling a crystalline mass is deposited, which is mixed with an alkali and distilled in a current of steam. The tetrahydride has the sp. gr. 1·1714 at 17°. The hydrochloride melts at 225° with decomposition. It is oxidised by platinum chloride. The nitroso-compound forms golden needles, and melts at 112°. A mixture of the nitrosamine with phenol and sulphuric acid gives an intense blue coloration with sodium hydroxide. W. C. W.

Isomeride of Glyoxaline. By E. BUCHNER (*Ber.*, **22**, 2165—2167).—The compound, $C_3H_4N_2$, obtained by heating acetylenedicarboxylodiazoacetic acid at 230—240° (this vol., p. 694) can be volatilised in a bath of diphenylamine vapour without decomposition, and a vapour-density determination by V. Meyer's method gives results agreeing closely with those required for the formula. The compound melts at 69—70°, boils at 184—185° under a pressure of 719 mm., exhibits feeble basic properties, and in aqueous solution has a neutral reaction. The *picrate* crystallises in slender, yellow needles; the *hydrochloride*, $C_3H_4N_2,HCl$, prepared by passing hydrogen chloride into an ethereal solution of the base, crystallises in colourless prisms, and is extremely hygroscopic; the *platinochloride*, $(C_3H_4N_2)_2,H_2PtCl_6$, crystallises in yellow prisms, decomposes without previous fusion when heated, and is readily soluble in water, soluble in alcohol; the *mercurochloride* is a white precipitate. On treatment with silver nitrate in the presence of ammonia, the *silver* compound, $C_3H_3N_2Ag$, is obtained; it is sparingly soluble in boiling water. Bromine reacts with the base in aqueous solution in the proportion of an atom to a molecule, and converts it into a *bromo*-derivative, which crystallises from water in glistening scales having a bromoform-like odour; it melts at 87—88°, and is soluble in cold water. The *methyl*-derivative, $C_4H_6N_2$, prepared by heating the silver compound with methyl iodide and ether in a closed tube at 120°, is a colourless oil with a strong pyridine-like odour, and in aqueous solution has a neutral reaction; its *platinochloride*, $(C_4H_6N_2)_2,H_2PtCl_6$, forms orange-red prisms, which melt at 198° with decomposition. In ethereal solution, the base gives a greenish-yellow colour with nitrous acid, and after some time white crystals, consisting probably of the nitrate, separate in small quantity, whilst the solution on evaporation gives a colourless, crystalline substance, which does not melt at 100°. Acetic and benzoic chlorides react energetically with the base; the *benzoyl*-derivative crystallises in colourless plates. In its properties, the base shows many similarities to the isomeric glyoxaline, and the author suggests that it may have the constitution  $\left.\begin{array}{l}CH{=}N\\ \vert\\ CH{:}CH\end{array}\right>NH$.

W. P. W.

Monosubstituted-derivatives of Pyrazole and Hydrogenated Compounds derived from them. By L. BALBIANO (*Gazzetta*, **18**, 354—379; compare Abstr., 1887, 1054).—Phenylpyrazole, $C_3H_3N_2Ph$, was prepared by the method previously described (*loc. cit.*). It is a golden-yellow, oily liquid, which at a low temperature solidifies to a mass of crystals melting at 11—11·5°. It boils at 246·5° (corr.), under a pressure of 765·4 mm. Its density at 16° is 1·1138, and at 99·7° = 1·0451 referred to water at 0°. The *platinochloride*, $C_9H_8N_2,H_2PtCl_6 + 2H_2O$, decomposes at 171°.

Phenylpyrazoline, $C_3H_5N_2Ph$, from phenylpyrazole. As this cannot be obtained directly by the action of epichlorhydrin on phenylhydrazine, it was prepared from phenylpyrazole by dissolving it in alcohol (10 to 15 parts), and adding sodium (0·5 part) in small pieces at a time to the boiling solution. This was then diluted with water, the alcohol removed by evaporation, and the residue extracted with ether. After the ethereal solution had been shaken up with an aqueous oxalic solution, it was dried with potash, evaporated, and the residue heated in a retort to 255°; unaltered pyrazole and some phenylpyrazoline passed over, and the residue, when carefully crystallised from light petroleum, yielded colourless tables belonging to the trimetric system, melting at 51·5—52°, boiling at 273·5—274° (at 765·5 mm.), and identical in every respect with the pyrazoline prepared from acraldehyde by E. Fischer's method.

Trimethylenephenyldiamine, $NH_2 \cdot C_3H_6 \cdot NHPh$, from phenylpyrazole. The oxalic acid extract of the ethereal solution mentioned in the preceding paragraph contains the *oxalate* of this base, which, on evaporating the solution, is obtained in small, colourless nodules, sparingly soluble in cold water. The *base* itself is a colourless liquid, insoluble in water, but soluble in alcohol and in ether. It has an ammoniacal odour, recalling that of aniline, boils at 276—278°, and does not solidify at −15°. The *hydrochloride*, $C_9H_{14}N_2,2HCl$, crystallises in tufts of needles, and is excessively soluble in water. The author compared this trimethylenephenyldiamine with that obtained from phenylpyrazole prepared from acraldehyde, and proved the two to be identical.

Paratolylpyrazole, $C_3H_3N_2{\cdot}C_6H_4Me[C_3H_3N_2 : Me = 1 : 4]$.—On heating epichlorhydrin (1 mol.) and paratolylhydrazine (2 mols.) dissolved in an equal weight of dry benzene, crystals of paratolylhydrazine hydrochloride are deposited; the mixture is then boiled for 6—7 hours, the benzene distilled off, and the residue heated at 140—150° in an oil bath, when a brisk reaction sets in, and water passes over. The product is distilled in a current of steam, and the yellow oil which passes over with the water is extracted with ether. The ethereal solution, after being extracted with dilute hydrochloric acid and evaporated, leaves the paratolylpyrazole, which is purified by recrystallisation from alcohol or from light petroleum. It forms slightly yellowish, lustrous plates, melts at 32·5—33°, and boils without decomposition at 258—259°, under a pressure of 756·9 mm. (corr.). It is only sparingly soluble in boiling water, but dissolves in concentrated hydrochloric acid, being reprecipitated on diluting the solution. On adding a fragment of sodium to the boiling alcoholic solution, acidifying with hydrochloric acid, and then adding potassium dichromate, an intense violet-red coloration is produced. The *platinochloride*, $(C_3H_3N_2{\cdot}C_6H_4Me)_2,H_2PtCl_6 + 2H_2O$ forms reddish-yellow, prismatic needles, sparingly soluble in cold water.

Ethylparatolylpyrazolammonium iodide, $C_7H_7{\cdot}C_3H_3N_2EtI$, obtained by heating paratolylpyrazole with ethyl iodide at 100—110° for 6 hours, forms hard, colourless, prismatic crystals, which melt at 104—105°, and are very soluble in water, but insoluble in ether.

Paratolylpyrazoline, $C_3H_5N_2{\cdot}C_6H_4Me\ [C_3H_5N_2 : Me = 1 : 4]$, from acraldehyde. This pyrazoline was prepared by E. Fischer's method. Acraldehyde (20 grams) dissolved in ether (50 grams) is added to a solution of paratolylpyrazole (45 grams) in ether (500 grams), the ether distilled off after 24 hours, and the residue mixed with dilute sulphuric acid (400 grams containing 2 per cent. acid). On distilling the mixture in a current of steam, the pyrazoline passes over, and on cooling separates in iridescent, colourless plates. It is soluble in alcohol, ether, and light petroleum, sparingly in hot water. It melts at 60·5°, and distils without decomposition at 281—282°, under a pressure of 757·9 mm. (corr.). It dissolves in concentrated hydrochloric acid, and is precipitated again unaltered on diluting the solution. Its acidified solution acquires a fine violet-red colour on the addition of potassium dichromate.

The paratolylpyrazoline, prepared from paratolylpyrazole in a manner precisely similar to that already described in the case of phenylpyrazoline, was found to be identical in every respect with that prepared from acraldehyde and paratolylhydrazine.

Trimethyleneparatolyldiamine, $NH_2{\cdot}C_3H_6{\cdot}NH{\cdot}C_6H_4Me$.—The oxalate of this base is obtained on evaporating the oxalic acid extract in the preparation of paratolylpyrazoline from the pyrazole, and crystallises in spherical groups consisting of minute needles; it melts with decomposition at 207—208°. The base is a yellowish liquid, which boils at 286—287°, and forms a crystalline mass when cooled to —15°. It is soluble in alcohol, ether, and dilute acids, but insoluble in water. It gives a reddish-brown coloration with potassium dichromate and dilute sulphuric acid. The *hydrochloride* is exceedingly soluble in water. This diamine was found to be identical in every respect with the trimethyleneparatolyldiamine obtained from the paratolylpyrazoline prepared by Fischer's method with acraldehyde.

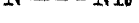
Orthotolylpyrazole, $C_3H_3N\cdot C_6H_4Me$ [$C_3H_3N_2 : Me = 1 : 2$], obtained from epichlorhydrin and orthotolylhydrazine in the way already described for the para-compounds, is a yellowish oil, boiling at 246·5 under a pressure of 754·1 (corr.). Its density at 0° = 1·0868, at 13° = 1·0746, and at 100·3° = 0·9984 referred to water at 0°. Unlike the corresponding para-compound, it does not take up hydrogen when its alcoholic solution is treated with sodium. The *platinochloride*, $(C_3H_3N_2\cdot C_7H_7)_2,H_2PtCl_6$, forms large, yellowish-red prisms, which melt at 200—201° with decomposition. It is but sparingly soluble in water.

Ethylorthotolylpyrazolammonium iodide, $C_7H_7\cdot C_3H_3N_2EtI$, crystallises in colourless needles, very soluble in water, insoluble in ether.

Orthotolylpyrazoline, $C_3H_5N_2\cdot C_6H_4Me$, prepared from acraldehyde in a manner precisely similar to that employed for obtaining the para-compound, is a colourless liquid, boiling at 271°, under a pressure of 759·5 mm. (corr.). Its density at 0° referred to water at 0° is 1·084. It is soluble in fuming hydrochloric acid, but is precipitated unaltered on the addition of water. Its aqueous solution gives an indigo-blue coloration with potassium dichromate and sulphuric acid.

Trimethyleneorthotolyldiamine, $NH_2\cdot C_3H_6\cdot NH\cdot C_6H_4Me$.—When orthotolylpyrazoline is dissolved in absolute alcohol and treated with sodium, it takes up hydrogen, and is converted into the diamine in the same way as the other pyrazolines. The oxalate crystallises in colourless nodules, consisting of minute needles. The base itself is a yellowish liquid, insoluble in water, but soluble in alcohol and ether. It boils at 280—282°. The *hydrochloride* crystallises in slender needles, which are exceedingly soluble in water, sparingly in alcohol.

These experiments show that epichlorhydrin reacts with the primary aromatic hydrazines, giving rise to a monosubstituted *pyrazole*, $C_3H_3H_2OCl + 2H_3N_2R = C_3H_3N_2R + H_2O + NH_4Cl + NH_2R$. That acraldehyde, on the other hand, gives rise to a *pyrazoline*, $C_3H_4O + H_3N_2R = C_3H_5N_2N + H_2O$. That the limited hydrogenation of the pyrazoles gives rise to the corresponding pyrazolines; whilst complete hydrogenation of either the pyrazoles or pyrazolines yields the corresponding substituted trimethylenediamine.

The author concludes by giving a table of the properties of the three pyrazoles described in the paper, and of their derivatives, and then discusses the probable constitution of the pyrazoles, which he believes to be 
$$\begin{array}{l} CH\cdot CH:CH \\ \| \qquad\quad | \\ N \text{——} NR \end{array}.$$

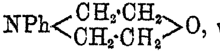
C. E. G.

Syntheses in the Oxazine Series. By L. KNORR (*Ber.*, **22**, 2081—2099).—In a previous paper (this vol., p. 905) it has been shown that morphine is probably a derivative of tetrahydroparoxazine, $NH<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>O$, and experiments have now been undertaken with the object of preparing derivatives of this hitherto unknown base. *Morpholine* (tetrahydroparoxazine) may be regarded as the "inner anhydride" of dihydroxyethylamine, $NH(CH_2\cdot CH_2\cdot OH)_2$, and can be obtained in small quantity by heating this base with hydrochloric acid at 160°, treating the product with alkali, and distilling with steam. It resembles piperidine in its physical and chemical properties.

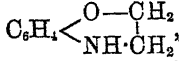
Hydroxyethylmethylamine, $NHMe\cdot CH_2\cdot CH_2\cdot OH$, is prepared by heating equivalent quantities of methylamine and ethylene chlorhydrin in aqueous solution at about 110° for 12—24 hours; the product is then evaporated with hydrochloric acid, and the concentrated solution distilled over solid potash. The first portion of the distillate consists of methylamine, but afterwards the hydroxy-base distils over in the form of a 30 per cent. aqueous solution; the yield amounts to about 80 per cent. of that theoretically possible. The complete dehydration of the base can only be effected with much difficulty. It separates as an oil on the addition of caustic potash to the aqueous solution, boils at 130—140°, and is readily soluble in water, alcohol, and ether. The *aurochloride*, $C_3H_9NO,HAuCl_4$, crystallises in anhydrous prisms, melts between 110 and 120°, and is very readily soluble in water.

Dihydroxyethyl-methylamine, $NMe(CH_2\cdot CH_2\cdot OH)_2$, is best obtained by heating equivalent quantities of ethylene chlorhydrin and hydroxyethylmethylaniline in aqueous solution for some hours at about 120°; the product is then treated with moist silver oxide to remove chlorine and distilled (compare Morley, *Ber.*, **13**, 223). It is a thick oil, which boils at 250—255°, does not distil with steam, and is very readily soluble in water. Methyl iodide combines with the base forming dihydroxyethyldimethylammonium iodide, from which the hydroxide can be obtained in the usual way; when heated, this decomposes with the formation of acetaldehyde and hydroxyethyldimethylamine. The *aurochloride* of this ammonium base, $C_6H_{16}NO_2,HAuCl_4$, crystallises in scales, melts at 233°, and is very readily soluble in hot water; the *platinochloride*, $(C_6H_{16}NO_2)_2,H_2PtCl_6 + H_2O$, separates from dilute alcohol in small crystals, which melt at 217—218°, and dissolve readily in water, but only sparingly in alcohol.

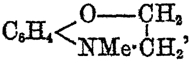
Methylmorpholine, $NMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>O$, is obtained by heating dihydroxyethylmethylamine with concentrated hydrochloric acid for 12 hours at 160°. The acid product is freed from symmetrical dichlorethane, which is always formed in small quantity during the reaction, by distillation with steam, and is then rendered alkaline, again distilled with steam, and the distillate treated with caustic potash in order to separate the base from its aqueous solution. It boils at 117° (thermometer in vapour), is readily soluble in water, alcohol, and ether, and resembles methylpiperidine in its chemical and physical properties. The *hydrochloride*, $C_5H_{11}NO,HCl$, crystallises from absolute alcohol in long hygroscopic prisms, and melts at 205°; the *platinochloride*, $(C_5H_{11}NO)_2,H_2PtCl_6$, crystallises from dilute alcohol in slender needles, and decomposes at 199°; the *aurochloride*, $C_5H_{11}NO,HAuCl_4$, crystallises in compact prisms, and melts at 183°; the *methiodide*, $C_5H_{11}NO,MeI$, crystallises in long needles; the *methochloride* is crystalline, and yields a crystalline *platinochloride*, and sparingly soluble *aurochloride*, $C_6H_{11}NO,MeCl,AuCl_3$. On treatment with moist silver oxide, the methiodide is converted into *methylmorpholinmethylammonium hydroxide*, which decomposes when heated, with the formation of acetaldehyde and hydroxyethyldimethylamine.

Hydroxyethylaniline (Demole, this Journal, 1874, 77) can readily be prepared by heating together, out of contact with the air, equivalent quantities of aniline and ethylene chlorhydrin for some hours at 110°. The syrupy product is extracted with water, and the solution after filtration from a compound, probably diethylenodianiline, which separates in flocks, is treated with aqueous potash; a mixture of bases is thus obtained, which on fractionation yields hydroxyethylaniline as chief product, together with some aniline and a small quantity of dihydroxyethylaniline. *Hydroxyethylaniline* boils at 286° (thermometer in vapour). When heated at 110° for several hours with ethylene chlorhydrin in molecular proportion, and some water, hydroxyethylaniline is converted into *dihydroxyethyl-aniline*, which boils above 350° with only slight decomposition, and is sparingly soluble in dry ether. Heated for some hours at 160—180° with fuming hydrochloric acid, this base yields a compound which seems to have the composition $OH{\cdot}CH_2{\cdot}CH_2{\cdot}NPh{\cdot}CH_2{\cdot}CH_2Cl$, and can be isolated by treating the product with cold aqueous soda, and extracting with ether. This intermediate product, when boiled for an hour with aqueous soda, or submitted to distillation, is converted into *phenylmorpholine*,  $NPh{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}O$, which is crystalline, melts at 53°, boils at 270°, is readily volatile with steam, and is insoluble in water, readily soluble in alcohol and ether. The *hydrochloride*, $C_{10}H_{13}NO,HCl$, and *aurochloride* were prepared; the latter crystallises in needles, and decomposes when boiled with water.

Hydroxyethylorthamidophenol is prepared by heating equivalent quantities of orthamidophenol and ethylene chlorhydrin with some water for several hours at 150°. It distils between 290—310°, is soluble in alkalis and acids, and is very sensitive towards oxidising agents, becoming rapidly dark-brown on exposure to air. The methoxy-derivative, *hydroxyethylorthanisidine*, $OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is formed by heating orthanisidine and ethylene chlorhydrin in molecular proportion in a sealed tube for 12—24 hours at 115—120°. This compound is a thick, colourless oil, boils at 295° (at 305° with thermometer in vapour), is sparingly soluble in water, readily soluble in the ordinary solvents, and has strong reducing properties. When either of these compounds is heated with fuming hydrochloric acid for several hours at 160°, it yields an intermediate product, *chlorethylorthamidophenol*, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CH_2Cl$, which can be extracted by ether from the solution after neutralisation, and on distillation, or when boiled for some time with aqueous soda in a reflux apparatus, is converted into phenomorpholine.

Phenomorpholine,  $C_6H_4<\begin{array}{l}O—CH_2\\ NH\cdot CH_2\end{array}$, is a colourless, mobile oil, of characteristic odour; it boils at 268° (thermometer in vapour), becomes red on exposure to light, and in its properties resembles tetrahydroquinoline. The *hydrochloride*, C_8H_9NO,HCl, crystallises in scales, is very hygroscopic, and melts at about 120°; the *nitrosamine* resembles that of tetrahydroquinoline, and gives Liebermann's reaction. Duparc (Abstr., 1887, 948) and v. Miller (this vol., p. 990) have described a base to which the formula here given to phenomorpholin has been assigned, but unless the compound obtained by them was impure, the two cannot be identical.

Hydroxyethylmethylorthanisidine, $OMe\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$, obtained from methylanisidine under conditions similar to those employed in the preparation of hydroxyethylorthanisidine, boils at 290° (thermometer in vapour), and when heated with fuming hydrochloric acid at 160°, yields an intermediate product containing chlorine; on boiling this with aqueous soda it is converted into methylphenomorpholine.

Methylphenomorpholine,  $C_6H_4<\begin{array}{l}O——CH_2\\ NMe\cdot CH_2\end{array}$, boils at 261° (thermometer in vapour), has a powerful odour recalling that of quinoline bases, is readily volatile with steam, and reduces gold and platinum chlorides. The *hydrochloride*, $C_9H_{11}NO,HCl$, crystallises in short, tetragonal scales, melts at 162°, and in solution gives a dark-red colour on treatment either with ferric chloride or nitrous acid.

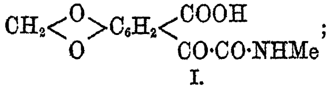
W. P. W.

Hydrastine. By M. FREUND and S. LACHMAN (*Ber.*, **22**, 2322—2328).—In a previous communication (this vol., p. 908), Freund described an oxidation product of hydrastinine to which he gave the name hydrastinic acid, and the formula $C_{11}H_{11}NO_5$. The authors now find that the acid previously examined still contained oxyhydrastinine, and that the true formula of the acid is $C_{11}H_9NO_6$. With nitric or chromic acids, this acid yields a crystalline compound (*loc. cit.*) of the formula $C_{10}H_7NO_4$. This substance melts at 233°, is soluble in glacial acetic acid, almost insoluble in ether. It dissolves when slightly warmed with alkalis, but is reprecipitated unchanged on the addition of acids. If, however, the alkaline solution is boiled until it becomes slightly turbid, and an acid is then added to the cooled solution, a new acid, $C_{10}H_{11}NO_6$, is precipitated, which melts at 224°. If this acid is again treated with potash, or the compound, $C_{10}H_7NO_4$, boiled for some time with concentrated potash, methylamine is evolved, and the potash salt of *hydrastic acid*, $C_9H_6O_6$, is formed. This acid crystallises from water in colourless needles, melts at 175°, and on continued heating loses the elements of water, and is converted into an anhydride. It is easily etherified by passing hydrogen chloride through its methyl alcohol solution. It is a bibasic acid, and when treated with fuming nitric acid is converted into methylenedinitropyrocatechol, $CH_2{:}O_2{:}C_6H_2(NO_2)_2$ (m. p. 101°), obtained by Hesse and Jobst (Abstr., 1878, 733) from piperonylic acid. Hydrastic acid must therefore have the constitution $CH_2{:}O_2{:}C_6H_2(COOH)_2$. Its easy conversion into the anhydride leaves little doubt that the two carboxylic groups are in the ortho-position to one another, but whether they are in positions 3 : 4 or 4 : 5, cannot yet be decided. The relationship of cotarnine to hydrastinine leaves little doubt that Roser's cotarnic acid similarly has the formula,

$$CH_2{:}O_2{:}C_6H(OMe)(COOH)_2.$$

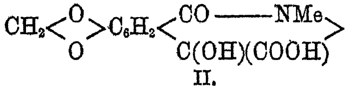
The compound $C_{10}H_7NO_4$, described above, is undoubtedly hydrastomethimide, $CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{CO}{CO} \gt NMe$, whilst the compound $C_{10}H_{11}NO_6$ is the methylamine salt, $CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{COO\cdot NH_3Me}{COOH}.$

The results obtained lead to one of the three following formulæ for hydrastinic acid :—



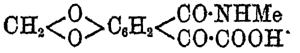
$$CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{COOH}{CO\cdot CO\cdot NHMe};$$

I.



$$CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{CO\text{——}NMe}{C(OH)(COOH)} \gt ;$$

II.



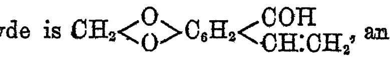
$$CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{CO\cdot NHMe}{CO\cdot COOH}\cdot$$

III.

Of these the last is most probably the correct one. Oxyhydrastinine would then have the constitution $CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{CO\cdot NMe}{CH_2\cdot CH_2}$, and hydrastinine that of $CH_2 \lt \genfrac{}{}{0pt}{}{O}{O} \gt C_6H_2 \lt \genfrac{}{}{0pt}{}{COH}{CH_2\cdot CH_2\cdot NHMe}$, and be a substituted piperonaldehyde. L. T. T.

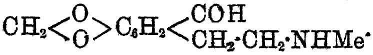
Hydrastine. By M. FREUND (*Ber.*, **22**, 2329—2339; see preceding Abstract).—In this research the author has extended to hydrastinine the experiments which Roser has made with cotarnine.

When heated with methyl iodide (either alone or in ethereal or chloroform solution), hydrastinine yields hydrastinine hydrochloride and *trimethylhydrastylammonium iodide*, $COH\cdot C_8H_8O_2\cdot NMe_3I$. This crystallises in yellow needles, soluble in boiling water or alcohol, and melts at 267°. Its formation shows that hydrastinine is a secondary amine. This ammonium-derivative yields, with hydroxylamine hydrochloride, an *oxime*, $OH\cdot N{:}CH\cdot C_9H_8O_2\cdot NMe_3I$, easily soluble in alkali, crystallising in yellow needles, and melting at 250°. The oxime is much more stable towards alkalis than the ammonium compound, and gives a dark reddish-brown, crystalline *platinochloride*. The corresponding chloride is similar in properties to the iodide, and melts at 245°. When trimethylhydrastylammonium iodide is warmed with aqueous alkalis, trimethylamine is evolved, and *hydrastaldehyde*, $C_9H_7O_2\cdot COH$, formed. This compound is soluble in alcohol, crystallises in rhombic plates, and melts at 78—79°. It is only very slightly soluble in boiling water, but volatilises in a current of steam. It is readily decomposed by acids, blue flocks being deposited. When reduced with sodium-amalgam, white needles, melting at 82—83°, are formed. The action of phenylhydrazine on hydrastaldehyde yields a compound, $C_9H_7O_2{\cdot}CH{:}N_2HPh$, crystallising in needles and melting at 103—104°. When oxidised with potassium permanganate, hydrastaldehyde yields a neutral crystalline compound melting at 158°, and an acid which appears to be hydrastic acid (see preceding Abstract). From the results obtained, the author considers the constitution of this group of compounds as definitely settled. Thus,

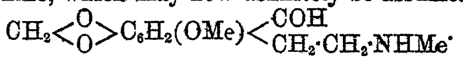
Hydrastaldehyde is 

$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{COH\\CH{:}CH_2},$$

and

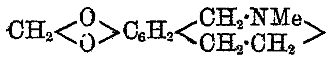
Hydrastinine, 

$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{COH\\CH_2{\cdot}CH_2{\cdot}NHMe}.$$

The proof of the existence of a benzene nucleus in hydrastinine and its derivatives confirms Roser's supposition of its existence in cotarnine, which may now definitely be assumed to have the constitution, 

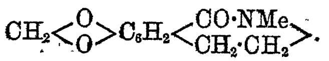
$$CH_2{<}\substack{O\\O}{>}C_6H_2(OMe){<}\substack{COH\\CH_2{\cdot}CH_2{\cdot}NHMe}.$$

The fact that the salts of hydrastinine and of cotarnine contain the elements of a molecule of water less than the free bases is probably due to the formation of a closed ring; and the same formation of a reduced isoquinoline nucleus probably takes place in the hydro- and oxy-derivatives of hydrastine. Their constitutions would then be:



$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CH_2{\cdot}NMe\\CH_2{\cdot}CH_2}{>};$$

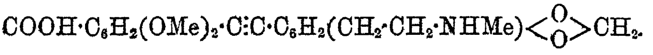
Hydrohydrastinine.



$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO{\cdot}NMe\\CH_2{\cdot}CH_2}{>}.$$

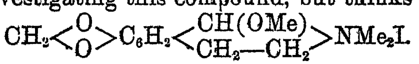
Oxyhydrastinine.

Hydrastine, the derivative of hydrastinine and opianic acid, has probably the formula,



$$COOH{\cdot}C_6H_2(OMe)_2{\cdot}C{:}C{\cdot}C_6H_2(CH_2{\cdot}CH_2{\cdot}NHMe){<}\substack{O\\O}{>}CH_2.$$

Decomposition would then take place at the point of treble linking, with the formation of an aldehyde in both the acid- and basic-derivative.

Whilst with methyl iodide, alone or in ethereal or chloroform solutions, hydrastinine yields trimethylhydrastlyammonium iodide, when heated with a solution of methyl iodide in methyl alcohol, it gives an isomeric compound soluble in boiling water or alcohol, and forming crystals melting at 230—232°. This is very stable towards alkalis, with aqueous solutions of which it may be heated without decomposition. The author is investigating this compound, but thinks it probably has the constitution 

$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CH(OMe)\\CH_2{-}CH_2}{>}NMe_2I.$$

L. T. T.

Mandragorine. By F. B. Ahrens (*Ber.*, **22**, 2159—2161; compare this vol., p. 1074).—Mandragorine can be purified by conversion into its crystalline mercurochloride and subsequent decomposition of this by hydrogen sulphide. It is a colourless, odourless, transparent, deliquescent substance, is soluble in the ordinary solvents, and when introduced into the eye produces mydriasis. The *hydrochloride* forms arborescent groups of deliquescent, serrated needles, the *platinochloride*, $(C_{17}H_{23}NO_3)_2,H_2PtCl_6$, crystallises in lustrous, yellow scales and melts at 193—194° with decomposition; the *mercurochloride*,

$$C_{17}H_{23}NO_3,HCl,4HgCl_2,$$

crystallises in lustrous scales or needles, melts at 159·5—160·5°, and is soluble in water and alcohol. The analytical numbers do not enable any definite conclusion to be drawn as to the amount of hydrogen present in mandragorine, since they agree equally well with those required for the formula $C_{17}H_{27}NO_3$. W. P. W.

The Existence of Avenine. By E. WRAMPELMEYER (*Landw. Versuchs-Stat.*, **36**, 299—301).—Sanson (Abstr., 1883, 914) found in oats an alkaloïd avenine, to which he ascribed the formula $C_{56}H_{21}NO_{18}$. The author could not obtain any alkaloïd from oats, and thinks it doubtful whether avenine exists at all. N. H. M

Crystallised Hæmoglobin. By MAYET (*Compt. rend.*, **109**, 157—159).—The author has modified Hoppe-Seyler's method for the preparation of crystallised hæmoglobin, and obtains a pure product and an increased yield. The corpuscles are washed with a solution containing 2·5 per cent. of pure anhydrous sodium sulphate, the volume used being 14 times the volume of the defibrinated blood operated on. Sodium sulphate tends to preserve the globules, whilst the sodium chloride which is usually employed partially destroys the stroma. The washed corpuscles are placed in a special receiver provided with a stopcock at the bottom, mixed with their own volume of water, and then with ether, in the proportion of one-fifth the total volume. The mixture is agitated for three minutes, and then kept at 0° for 24 hours, when it separates into a layer of hæmoglobin solution and a layer of stromas emulsified with the ether. The hæmoglobin is drawn off and gradually mixed with one-fifth its volume of pure absolute alcohol. A higher proportion decomposes part of the hæmoglobin. After filtration the alcoholic liquid is cooled to −14° in an éprouvette, and gradually remelted. The imperfect crystals thus obtained are drained and redissolved in just sufficient water at 35°, again mixed with alcohol, and cooled as before. The hæmoglobin is obtained in crystals as much as 1·5 mm. in length.

A much better result is obtained by using benzene instead of ether. The washed corpuscles are agitated with their own volume of water and one-fifth of the total volume of pure benzene, and then cooled below 8°, but not below 5°.

Benzene causes the separation of the colouring-matter, and has the advantage over ether that it produces no decomposition. The liquid separates into three layers, one vermilion in colour, and containing almost pure hæmoglobin, a second dull-red and consisting of the same liquid mixed with globular stromas, and the third yellowish-white, and consisting of benzene emulsified with the fatty matter of the corpuscles. The two lower layers are drawn off and mixed with alcohol, filtered, cooled, &c., as already described. C. H. B.

Ethereal-derivatives of Albuminoïds. By H. SCHRÖTTER (*Ber.*, **22**, 1950—1954).—Witte's peptone, which according to the investigations of Kühne, Chittenden, and Neumeister, consists of a mixture of various albuminoses, after having been purified by precipitating its solution in dilute acetic acid, first with a concentrated solution of ammonium sulphate, and then with alcohol, is obtained in the form of a white powder, which softens at 130°, and decomposes at a higher temperature.

The product thus obtained from 50 grams of peptone, is dissolved in the calculated quantity of 10 per cent. soda, and the solution shaken with benzoic chloride (50 grams) in the cold, the mixture being kept alkaline; heat is developed, and the reaction is at an end in a very short time, a white substance separating from the solution. After neutralising with acetic acid, the granular precipitate is washed with water, digested for a long time with a little alcohol, which dissolves sulphur compounds, and the residue treated twice with 10 per cent. soda and benzoic chloride (150 grams) as before. The solution is then almost neutralised with acetic acid, the precipitate washed with water, dried on porous plates, and extracted with boiling 60 per cent. alcohol. A considerable portion remains undissolved, and on cooling the filtered solution a colourless substance separates in microscopic crystals. The yield of this product is 18 per cent. It is insoluble in water, and only sparingly soluble in cold, but readily in hot alcohol; it melts at about 208—215° with decomposition, gives the biuret reaction, and is free from sulphur. Its composition is $C = 59{\cdot}75$, $H = 5{\cdot}9$, and $N = 11{\cdot}85$ per cent., as the average of analyses made with five different samples, and it contains 51·3 per cent. of benzoyl.

The alcoholic mother-liquors from the substance first described, when evaporated under reduced pressure, give a yellow, deliquescent powder. This product separates as a flocculent precipitate when its cold, 95 per cent. alcoholic solution is mixed with ether. The yield is 10 per cent. It deliquesces and turns yellow on exposure to the air, gives the biuret reaction distinctly, is free from sulphur, and readily soluble in warm alcohol, but insoluble in water. Analyses gave, on the average, $C = 54{\cdot}9$, $H = 5{\cdot}5$, and $N = 11{\cdot}19$ per cent., and 45·5 per cent. of benzoyl.

The ethereal alcoholic mother-liquors from the preceding compound, when evaporated at a moderate temperature, yield a syrupy residue which gradually solidifies to a mass of slender needles. The yield is 6 per cent. This crystalline product is colourless, and does not melt below 230°, although it turns brown at 190°; it is free from sulphur, gives the biuret reaction only very slightly, and is insoluble in water, alkaline carbonates, and cold alkalis, but readily soluble in alcohol. Analyses gave the following results:—$C = 61{\cdot}6$, $H = 4{\cdot}25$, $N = 10{\cdot}87$, and benzoyl 61 per cent. F. S. K.

Physiological Chemistry.

Reduction of Oxyhæmoglobin in the Heart. By S. HANDLER (*Zeit. Biol.*, **26**, 233—258).—The analysis of the gases of the blood entering and leaving such a small organ as the heart of the frog or tortoise being out of the question, the spectroscopic method was employed. An ingenious apparatus, described and figured, was used; a solution consisting of either rabbits' or calves' blood, with 9 parts of saline solution, was kept in the heart: in some cases the organ beat spontaneously; in others only in response to stimulation; the heart was placed in connection with a two-way cannula, and the whole suspended in a chamber connected with a mercurial reservoir, by raising or lowering which, fluid could be drawn into or drawn out of the heart, and then immediately subjected to spectroscopic examination in a part of the apparatus that was transparent. If the oxyhæmoglobin were not fully reduced, the solution was returned to the heart, examined again at intervals, and a note made of the time taken for the reduction to occur. The so-called auto-reduction that occurs in shed blood may be postponed indefinitely by a temperature of 0°, or by protection from atmospheric microbes. The authoress confirms Yeo's observation, that it is a ferment process. The other observations she makes are also very largely confirmatory of Yeo's work (*J. Physiol.*, **6**, 93).

The turtle's heart reduces oxy-hæmoglobin much more quickly than the frog's heart (5—15 : 15—80 minutes). With regard to the influence of temperature on the rate of reduction, contradictory results were obtained. The most marked fact, however, was that an increase in the rate of the heart's beat, and of the rate of reduction always go together; but the latter is independent of the work done by the heart as tested by filling the reservoir with different liquids—mercury, oil, blood, &c. Kronecker obtained much the same result with skeletal muscles; he found that fatigue depends on the frequency of contraction more than on the actual amount of work done. W. D. H.

The Digestibility of Boiled Milk. By R. W. RAUDNITZ (*Zeit. physiol. Chem.*, **14**, 1—14).—The difference of digestibility between boiled and fresh milk is a matter of great importance with regard to the feeding of infants. The present experiments were carried out on a dog, and are merely preliminary to others to be undertaken on a more extended scale.

The animal was fed for the period of a few days on unboiled milk, and then for another period on an equal quantity of the same milk (boiled). The amounts of lime, nitrogen, and fat were estimated both in the milk and in the excreta (urine and fæces). The animal was also weighed daily; a second series of experiments was similarly conducted, but the results appear to be of less value, as by that time the dog seemed to have ceased growing, and had attained its adult state.

When rennet was added to boiled milk, it was found that the clot consisted of fine flocculi which could be separated by filtration; there was no large coherent coagulum as in fresh milk.

The following abbreviated table of one series of experiments will illustrate the general plan of the experiments:—

Food.	Nitrogen.			
	In food, in grams.	Percentage		
		In urine.	In fæces.	Retained in body.
Fresh milk for three days	15·6	77·29	13·27	9·44
Boiled milk for two days	10·4	75·71	18·56	5·73

	Fat.		CaO.	
	In food, in grams.	Percentage in fæces.	In food, in grams.	Percentage in fæces.
Fresh milk for three days...............	105·3	5·59	5·18	37·82
Boiled milk for two days	70·2	3·72	3·45	62·68

The following general conclusions are drawn:—

1. The nitrogen is always better assimilated when the milk is fresh. The lessening of the absorption of nitrogen when the milk is boiled can only be caused by the boiling. Two other possible reasons—(1) the keeping of the milk for several days before it was used; (2) the rebelling of the animal's alimentary canal against a diet composed solely of milk—are excluded by counter experiments, for details of which the original memoir must be consulted.

2. With regard to the fat, boiling makes, apparently, little or no difference.

3. The experiments on the absorption of lime are not regarded as sufficiently numerous to enable conclusions to be drawn from them.

Other experiments are promised in which this question is to be investigated with animals whose skeleton is undergoing the ossification process.

W. D. H.

Digestion of Beans in the Human Alimentary Canal. By W. Prausnitz (*Zeit. Biol.*, 26, 227—232).—A man was fed on 500 grams of beans daily for three days, together with small weighed quantities of fat, meal, salt, vinegar, and beer. The urine and fæces during this time were examined,

The total fæces contained 18·3 per cent. of the food weighed as dry material, 30·3 per cent. of the nitrogen of the food, 17·6 per cent. of its organic, and 28·3 per cent. of its inorganic constituents. The urine contained 44·16 grams of nitrogen; this, added to the nitrogen of the fæces, gave 58·4 grams as the output of nitrogen, the intake being 53·6 grams. This result is compared with similar observations on other forms of food; in animal food there is naturally less waste; but even with other forms of vegetable food beans compare most unfavourably. W. D. H.

Influence of Chlorides on the Composition of the Gastric Juice. By H. Girard (*Arch. de Physiol.*, 1889, 595—599).—Rectal injection of sodium chloride has a peptogenic action, increasing the amount of gastric juice secreted, and the percentage of hydrochloric acid, and, to judge by its activity in dissolving fibrin, the pepsin is increased also. The experiments were performed on a dog, and the following table gives some of the results obtained:—

Experiment.	Amount of juice collected before injection.	Percentage of hydrochloric acid.	Amount of juice collected ¼ hour after injection.	Percentage of hydrochloric acid.
1..........	3 c.c.	0·03	11 c.c.	0·1
3..........	4 "	0·05	12 "	0·3
5..........	7 "	0·1	9 "	0·165
10	1 "	traces	13 "	0·3

Experiments were also performed with the chlorides of calcium, magnesium, and potassium, but the same results did not follow, for although the juice obtained was very thick and rich in pepsin, the acid was not increased, and was even absent in some cases.

W. D. H.

The Influence of Artificial Gastric Juice on the Acetous and Lactic Acid Fermentations. By F. O. Cohn (*Zeit. physiol. Chem.*, **14**, 75—105).—Of the views held concerning the origin of the hydrochloric acid in the gastric juice, one of the most generally accepted is that lactic acid formed from carbohydrates, liberates hydrochloric acid, by acting on sodium chloride (Ewald). At the same time, it is well known that acidity stops fermentative processes, and it is therefore important to determine accurately what influence gastric juice exerts on the acetic acid and lactic acid fermentations, and what concentration of hydrochloric acid stops the fermentation.

In the present research an artificial gastric juice was made with the *Pepsinum germanicum* of Witte-Rostock; the micro-organisms of the acetic and of the lactic fermentations were grown in suitable saline media. This was titrated with normal sodium hydroxide solution before and after infection with the micro-organisms in question.

The influence on the rate of fermentation of (1) pepsin, (2) hydrochloric acid, (3) pepsin and hydrochloric acid, and (4) hydrochloric acid in the presence of peptone, was investigated; some experiments were also made to determine the amount of decomposition of phosphates brought about by hydrochloric acid.

The results obtained were as follows:—

(1.) Pepsin does not hinder either the acetic or the lactic acid fermentations, but it appears to be a good nitrogenous pabulum for the organisms.

(2.) Even traces of hydrochloric acid hinder the acetic fermentation. The lactic fermentation is stopped by just so much hydrochloric acid as is necessary to change the phosphates (which are present in the nutritive liquid for the proper growth of the *Bacterium acidi lactici*) into chlorides. The fermentation was thus probably hindered by the hydrogen phosphate thus liberated.

(3.) Pepsin and hydrochloric acid together act in the same way as hydrochloric acid alone, only not quite so powerfully.

(4.) Hydrochloric acid in the presence of (probably combined with) peptone, does not hinder the fermentations at all. It is also useless in aiding the digestion of albumin by pepsin.

(5.) The acetic acid fermentation is hindered by hydrochloric acid when sufficient has been added to liberate from 0·5 to 0·7 parts per thousand of hydrogen phosphate from the phosphates present.

W. D. H.

Formation of Nitrous Acid and Nitric Acid in Saliva from Formaldehyde and Ammonia. By C. Wurster (*Ber.*, **22**, 1901—1908; compare Abstr., 1886, 298).—Experiments have shown that fresh saliva does not, as a rule, contain nitrous acid, although in exceptional cases it is present both in saliva and in perspiration, especially when the other animal juices and the urine contain an abnormally large quantity of nitrates. When saliva is kept for a few hours, or boiled, or even filtered, it undergoes change, and after having been mixed with glacial acetic acid or dilute sulphuric acid it gives Griess's reaction for nitrites; fresh saliva, collected in glacial acetic acid gives the reaction of hydrogen peroxide only. If fresh saliva (10 c.c.) is collected in 20 per cent. sulphuric acid (3 drops), the reactions of active oxygen, as a rule, disappear, and tetramethylparaphenylenediamine paper is not coloured by it; nitrous acid also cannot be detected, but nitric acid can be shown to be present by the diphenylamine reaction.

Salts, especially sodium chloride, hasten the formation of nitrates in saliva; if nitrites are already present, the reaction appears quickly on adding acetic acid, but rather more slowly on the addition of sulphuric acid, a proof that the oxidising agent in saliva is not, as a rule, nitrous acid.

A number of experiments showed that, when saliva (10 c.c.) is warmed with baryta under reduced pressure, the ammonia evolved neutralises, as a rule, 4 c.c. of N/50 acid, a quantity corresponding with 0·1336 gram of ammonia per litre of saliva. The quantity of ammonia in the saliva of different persons is almost constant, although the quantity of active oxygen varies very considerably, but the saliva from one man contained regularly about 0·1904 gram of ammonia per litre.

Saliva which contains but little active oxygen, as shown by the tetramethylparaphenylenediamine reaction, gives the normal quantity of ammonia, but when a large quantity of hydrogen peroxide is present the whole of the ammonia is obtained on distillation only when the saliva is clear and contains but a small quantity of salts. The formation of nitrous acid commences soon after expectoration in turbid saliva, in saliva from weak persons, and in that excreted in the summer heat, and the quantity of ammonia obtained on distillation is diminished to a corresponding extent. If the saliva is collected in sodium chloride solution or in dilute sulphuric acid, the quantity of ammonia obtained on distillation is decreased according to the quantity of hydrogen peroxide present; the residue contains nitrites in those samples distilled with sodium chloride, but nitrates when sulphuric acid has been added.

In the hot summer months, saliva yields less ammonia on distillation; even when ferrous hydroxide or pyrogallol is added to remove the active oxygen, although the quantity of ammonia obtained is thereby slightly increased, it is still less than that obtained in winter. The quantity of ammonia which disappears on adding sodium chloride or sulphuric acid is always the same in both cases, and is generally equal to 1 c.c. of N/50 acid, but frequently amounts to 2 c.c. or 3 c.c.; this phenomenon can be explained by assuming that ammonia, both in acid and alkaline solutions is oxidised by the active oxygen to nitrous oxide, which is then principally converted by the passive oxygen into nitrous acid in alkaline solution, in acid solution into nitric acid. Fresh saliva (10 c.c.), and saliva collected in sodium chloride solution, neutralise, as a rule, when directly titrated, 6 c.c. of N/50 acid; it must be assumed, therefore, that in the process of titration the same oxidation of ammonia takes place as on boiling or keeping. When saliva is previously titrated, it yields less ammonia on subsequent distillation than fresh saliva, and saliva free from active oxygen has a greater alkalinity (10 c.c. neutralise 7 to 13 c.c. N/50 acid) than saliva rich in active oxygen.

Saliva which has been kept for 24 hours at a summer heat, and in which the nitrites have been reduced by micro-organisms, has an alkalinity of almost 7 to 9 c.c. of N/50 acid, and contains a correspondingly larger quantity of ammonia; the nitrates also disappear when saliva is kept at a summer heat, but not until after two or three days.

The above experiments were carried out with saliva which was obtained without irritating the mucous membrane, and taken while in a state of rest.

Saliva obtained simply by chewing and sucking movements is thin and poor in organic constituents, and frequently contains large quantities of active oxygen, but that obtained by irritating the mucous membrane with sodium chloride, in quantities sufficient to be painful, contains no active oxygen and a much smaller quantity of ammonia than usual; the saliva secreted under the influence of irritants is thick, contains a large quantity of mucus and saccharifies starch paste about three times as quickly as normal saliva. As the irritation passes off, nitrous acid appears in the saliva, and its quantity increases as that of the mucus decreases; subsequently both ammonia and active oxygen appear, and the saliva regains its original composition in 3 to 15 minutes, according to the intensity of the irritation, after the source of irritation is removed. The saliva secreted at the period of greatest irritation contains, besides mucus, nitrates and carbamide; in one case, 200 c.c. of saliva yielded 0·09 gram of carbamide and 3·1 to 5·1 milligrams of nitric oxide, determined by Schultze's method, whilst one sample (115 c.c.) containing nitrites gave 28·4 milligrams of nitric oxide. The quantity of ammonia present is reduced very considerably, 10 c.c. of the saliva neutralising only 1 c.c. of N/50 acid; a few observations seem to show that the base which remains is not ammonia itself, but some derivative thereof. The disappearance of both active oxygen and ammonia from saliva on the appearance of mucus is so much the more remarkable, since it has been previously shown that the caseïn-like substance formed by the oxidation of egg albumin by hydrogen peroxide is converted into a mucus-like substance (mucin) in presence of ammonia and hydrogen peroxide (compare Abstr., 1887, 683).

Saliva containing both carbamide and nitrous acid colours Griess's red reagent (α-naphthylamine and sulphanilic acid) bluish-violet.

When the uppermost layers of the mucous membrane of the mouth are coagulated by repeatedly treating with absolute alcohol or tannin, and then removed, the metallic taste of hydrogen peroxide in the saliva becomes even disagreeably perceptible, and lasts in some cases for more than two days.

That the oxidising substance in saliva is hydrogen peroxide, and not nitrous acid, follows from its behaviour with potassium iodide starch paper containing sodium chloride. If a saliva, rich in active oxygen, but which does not act on Griess's reagent, is treated with potassium iodide starch paste and glacial acetic acid, a yellow or yellowish-brown solution is obtained on shaking, as is the case with hydrogen peroxide. If, however, the saliva is placed on the surface of the glacial acetic acid iodine solution, a yellowish-brown ring is first formed at the surface of contact, and then the saliva gradually turns reddish, and finally blue. Glacial acetic acid seems to be the only substance which prevents the oxidation of ammonia in saliva by the hydrogen peroxide for any length of time; oxidation takes place quickly in presence of dilute hydrochloric or sulphuric acid.

Although the presence of hydrogen peroxide cannot be proved by the chromic acid reaction, the author is of the opinion that hydrogen peroxide is the oxidising agent in saliva.

Hydrogen peroxide which has been filtered 20 times through manganese dioxide still contains as much active oxygen as can be shown by the tetramethylparaphenylenediamine reaction to be present under favourable conditions in saliva, perspiration, and certain vegetable juices.

Hydrogen peroxide which has been kept for hours in contact with platinum black and silver oxide still shows an oxidising action equal to that of a N/250 solution of iodine. F. S. K.

Muscle Pigments. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **14**, 106—108).—This is a continuation of the polemical discussion on the subject of myohæmatin (compare this vol., pp. 633, 1024).

W. D. H.

Animal Chromatology. By C. A. MacMunn (*Quart. J. Micros. Soc.*, **30**, 51—96).—This article describes a number of spectroscopic observations on the pigments and coloured tissues of many invertebrate animals selected from the classes of the echinoderms, worms, polyzoa, ascidians, cœlenterates, and crustaceans. The principal absorption-spectra are figured. In conclusion, an admirable account of the class of pigments called lipochromes or luteïns is given, together with some criticisms on Krukenberg's observations. W. D. H.

A Crystalline Acid from Pig's Bile. By E. Bergeat (*Chem. Centr.*, 1889, i, 812).—If pig's bile be almost completely precipitated by neutral plumbic acetate, and the yellow precipitate exhausted with alcohol, this solution concentrated, diluted with water, and ether added, a white, crystalline powder separates. It is readily soluble in alcohol, sparingly soluble in water, insoluble in ether, light petroleum, and chloroform. It forms amorphous sodium and lead salts, from which it may be again separated by the addition of acetic acid. About 5—10 per cent. may be obtained from the dry bile.

J. W. L.

The Stromata of Red Corpuscles. By W. D. Halliburton and W. M. Friend (*J. Physiol.*, **10**, 522—549).—The method found best for the preparation of the stromata of mammalian red corpuscles was that introduced by Wooldridge (*Du Bois Reymond's Archiv.*, 1881, 387). The stromata were then examined by the methods already used in the investigation of lymph-cells (Abstr., 1888, 974), the proteïds present being the chief point of the research. The only proteïd present of the four existing in typical cells, such as white blood-corpuscles, is the globulin which coagulates at 75° (cell globulin). This has fibrinoplastic properties, and is probably identical, as in lymph-cells, with fibrin-ferment. The absence of nucleïn and nucleo-albumin is interesting, as the mammalian red corpuscles possess no nucleus; chemically as well as morphologically they have lost this distinctive character of animal cells.

The presence of fibrin-ferment in the red discs suggests the question whether they contribute to the formation of fibrin in coagulation, as it usually occurs in shed blood. There is certainly no necessity to suppose that they shed out any ferment, as a rule, since they undergo disintegration much more slowly than the other formed elements of the blood; but it is nevertheless possible that under certain circumstances they may assist in the formation of fibrin, and that Landois's stroma-fibrin may be possibly accounted for in this manner. Bonne has recently suggested that in cases of disease in which the red blood-corpuscles are disintegrated within the blood-vessels (hæmoglobinæmia), the febrile disturbance that accompanies this condition may be due to the presence of fibrin-ferment derived from the stromata of the discs so dissolved. W. D. H.

Physiological Action of Hydrocyanic Acid. By N. GRÉHANT (*Compt. rend.*, **109**, 502—503).—Experiments were made on dogs in two ways—(1) by successive injections of amygdalin and emulsin; (2) the injection of very dilute hydrocyanic acid (0·25 per cent.). 2·2 c.c. of the dilute acid injected into the jugular vein of a dog was sufficient to cause death in 9·5 minutes. The symptoms follow one another in this order: convulsions, insensibility of the cornea, cessation of respiration, stoppage of the heart. The heart continues to beat for several minutes after respiration has ceased; in the case of frogs, the heart's action may continue for more than an hour after the animal has ceased to breathe. C. H. B.

The Relation between the Chemical Constitution and Physiological Action of certain Sulphones. By E. BAUMANN and A. KAST (*Zeit. physiol. Chem.*, **14**, 52—74).—After Kast (*Berlin klin. Woch.*, 1888, No. 16) had shown that sulphonal (diethylsulphonedimethylmethane) has a hypnotic action, it became a matter of interest to determine how far other similar compounds acted in the same way, especially whether it was the ethyl- or methyl-groups, or the sulphur-containing radicles of the sulphonal which were the most important. The disulphones fall into three groups, which may be represented by the general formulæ (1) $CH_2(SO_2R)_2$, (2) $CHR'(SO_2R)_2$, and (3) $CR'R''(SO_2R)_2$, R, R', and R'' being univalent alcohol-radicles, and may be either different or identical.

The following substances were investigated:—

Diethylsulphone was given to a dog of 6 kilos. body weight in doses of 5 and 7 grams. It had no action, and was excreted in great part unchanged in the urine. Ethylenediethylsulphone.—This was similarly investigated, and was found to be excreted unchanged, and had no action. Methylenedimethylsulphone, methylenediethylsulphone, and ethylidenedimethylsulphone all behaved in the same way.

Methylenedimethylsulphone, $CH_2(SO_2Me)_2$, is prepared by acting with methyl mercaptan on methylene chloride and aqueous soda, and oxidising the sulphide, $CH_2(SMe)_2$, so formed, with permanganate. It crystallises in large, transparent tables, melts at 142—143°, and volatilises unchanged. It yields a bromo-derivative, $CBr_2(SO_2Me)_2$, which crystallises in needles and melts at 234°.

Ethylidenedimethylsulphone, $CHMe(SO_2Me)_2$, prepared from aldehyde and methyl mercaptan, crystallises in cauliflower-like masses, melts at 122°, and dissolves in about 140 parts of cold water. In doses of 3 grams, given to a dog weighing 9½ kilos., it produced sleep, but rather less powerfully than similar doses of sulphonal. Small quantities of the drug were found in the urine.

Propylidenedimethylsulphone, $CHEt(SO_2Me)_2$, prepared from propaldehyde and methyl mercaptan, crystallises in large, transparent tables, melts at 97°, and dissolves in 90 parts of water at 15°. It had a slight hypnotic action, and was partly excreted as such in the urine.

Propylidenediethylsulphone, $CHEt(SO_2Et)_2$, crystallises in long needles or prisms, melts at 77°, and dissolves in 126 parts of water at 15°. It produced a condition resembling drunkenness, and finally sleep. The animals remained in this condition for some days, so that its effects are more lasting than those of sulphonal.

Dimethylsulphonedimethylmethane, $CMe_2(SO_2Me)_2$, which crystallises in large, transparent tables, melts at 118°, and dissolves in 140 parts of cold water, produced slight sleep in dogs; but the same doses had no effect on men.

Dimethylsulphonemethylethylmethane, $CMEt(SO_2Me)_2$, which crystallises in well-formed, transparent prisms and melts at 74°, had a slight hypnotic effect, lasting only a short time (four hours).

Dimethylsulphonediethylmethane, $CEt_2(SO_2Me)_2$, which crystallises in long needles and plates, melts at 132—133°, and dissolves in 840 parts of water at 15°, and in 20 parts at 100°, but more readily soluble in alcohol, acted almost precisely in the same way as sulphonal, with which it is isomeric, and both are found in the urine in traces only.

Diethylsulphonemethylethylmethane (*Trional*), $CMeEt(SO_2Et)_2$, prepared from methyl ethyl ketone and ethyl mercaptan, crystallises in lustrous tables, melts at 76°, and dissolves in 320 parts of cold water. It also acts like sulphonal, but could not be detected in the urine.

Diethylsulphonediethylmethane (*Tetronal*), $CEt_2(SO_2Et)_2$, forms lustrous tables and plates, melts at 85°, and dissolves in 450 parts of cold water. It is the most strongly hypnotic of all the sulphones examined.

The following general conclusions are drawn:—1. That the disulphones which pass wholly unchanged into the urine are not hypnotic. 2. That of the disulphones which undergo change in the body, those containing the ethyl-radicle are the most powerful hypnotics, and that the intensity of their action increases with the number of ethyl-radicles present. 3. The group SO_2 as such is of no account. 4. The methyl-group has little or no hypnotic action. W. D. H.

Glycogenesis in Icterus. By A. DASTRE and M. ARTHUS (*Arch. de Physiol.*, 1889, 473—483).—Experiments on dogs were undertaken to determine in what manner the glycogenic function of the liver is altered when the secretion of bile is altered quantitatively by the production of icterus by mechanical retention. For this purpose, a partial icterus was caused by the ligature of only one of the primary divisions of the bile duct. The liver thus consisted of two parts, one healthy, the other icteric. These were examined when the animal was killed, usually 15 or 16 days after the operation. The carbohydrate material was estimated as sugar, and originally consists partly of sugar, but for the most part of glycogen. In some cases, the glycogen was directly estimated by Külz' method. Both methods yielded the same result, that is a lowering of glycogenic activity in the icteric portions of the liver, the proportion of the glycogen there to that in the healthy parts of the liver being 12 or 13 to 10.

This modification of the glycogenic function, even within these somewhat narrow limits, must exercise an appreciable effect on nutrition, and may help to explain the symptoms experienced in cases where jaundice is produced by merely mechanical causes.

W. D. H.

Albumose isolated from Anthrax Cultures. By E. H. Hankin (*Brit. Med. Jour.*, 2, 1889, 811—812).—An albumose was separated from anthrax cultures by precipitation with alcohol; the precipitate was freed from ptomaïnes by washing with alcohol. Solutions of this precipitate were injected ~~into the circulation of rabbits~~ and mice; when these animals were subsequently inoculated with virulent anthrax cultures, they were found to be protected. It was found, however, that such immunity against the disease was conferred only when very minute doses of the albumose were administered namely, from one five-millionth to one ten-millionth of the body weight of the animal. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Presence of Ammonia and Nitrous Acid in Potable Water. By J. E. Enklaar (*Rec. Trav. Chim.*, 8, 327—328).—The author made a number of experiments in order to ascertain the origin of the nitrous acid which is formed in potable water, whilst the quantity of ammonia gradually becomes less. The conclusions at which he arrived are as follows:—No oxidation takes place when the water is boiled before the experiment; it occurs to a far less extent in distilled water.

The nitrous acid is formed by the oxidation of ammonia under the influence of microbes probably identical with the bacteria which play such an important part in nitrification. These microbes do not seem to develop in distilled water, but they multiply rapidly in water containing calcium carbonate and organic matter; they are killed or paralysed by free acids. The nitrous acid does not appear in the water until some days after the introduction of the oxidising microbes. F. S. K.

Relation between the Intensity of Radiation and the Decomposition of Carbonic Anhydride by Plants. By C. Timiriazeff (*Compt. rend.*, 109, 379—382).—A beam of sunlight directed by a heliostat was allowed to fall on plants in such a way that they received radiation of varying intensities, full exposure to sunlight being taken as the unit. The gas evolved was measured and analysed.

The rate of decomposition at first increases rapidly with the intensity of the radiation, then increases more slowly, and becomes constant at a point considerably below insolation, the curve being parallel with the axis of the abscissæ which represent the intensity of the radiation. These results confirm Kreusler's earlier experiments; the character of the curve is probably due to a relation between the proportion of the radiation absorbed by the chlorophyll (20 to 25 per cent. of that incident on the leaves) and the proportion (not more than

5 per cent.), which is actually converted into chemical work in the leaves. C. H. B.

Carbohydrates as Oxydation-products of Vegetable Albumin. By W. PALLADIN (*Chem. Centr.*, 1889, i, 811, from *Ber. deut. bot. Gesell.*, 7, 126—130).—The author holds that the transitory formation of starch, during the germination of seeds, occurs at the expense of the albumin, asparagine being formed at the same time. After this state is perfected and the starch has disappeared, dark plants accumulate asparagine, whilst in light plants the asparagine is reconverted into albumin.

The author has already (this vol., p. 642) shown that the formation of asparagine is accompanied by an assimilation of oxygen, and in consequence of the oxidation of albumin. The author has also previously shown that the ratio $CO_2 : O_2$ during the respiration of growing organs is less than unity, and that therefore the cell formation is accompanied by an absorption of oxygen, and he concludes from these facts that the carbohydrates are products of the incomplete oxidation of albumin. If the transitory formation of starch is accompanied by an absorption of oxygen, then the ratio $CO_2 : O_2$ must be less in the case of the respiration of the germinating leguminosæ than in that of the cereals. J. W. L.

Lignin. By G. LANGE (*Zeit. physiol. Chem.*, **14**, 15—30).—Payen (*Compt. rend.*, 8, 51) first showed that wood contained 10 per cent. more carbon than cellulose; the substance which thickens the walls of cells and vessels he termed "incrusting material," and found it was removable by nitric acid. F. Schulze (*Chem. Centr.*, 1887, 321), called this substance lignin, and gave it the empirical formula $C_{38}H_{24}O_{20}$. Other observers since then (Fremy, Hoppe Seyler, and others) have considered that the substance in question is a mixture. Thomsen (*Annalen*, **138**, 1) found that by the use of sodium hydroxide of sp. gr. 1·1 he was able to separate one of the constituents of lignin, which he called wood-gum: this is an isomeride of cellulose.

Wood-gum, however, does not exist as such in the wood; it is soluble in water; but water will not extract any wood-gum from wood; therefore it must be formed by the action of the alkali.

In the present research, lignin was prepared both from beech and ash wood. The method closely followed that of Thomsen; great care being taken to thoroughly wash the substances dealt with with a large number of reagents in which they were insoluble. The product was finally fused with alkali, and the products examined. The results may be briefly stated:—The products obtained are (1) Cellulose; (2) two kinds of lignic acid from each kind of lignin; these differ in elementary composition and in certain reactions; their chemical constitution has still to be worked out. (3) Formic acid, acetic acid, and traces of higher organic acids. (4) Protocatechuic acid, catechol, ammonia, and traces of higher bases. (5) A crystalline substance in very small quantities which has yet to be investigated. W. D. H.

Oleo-gum-resin secreted by Araucarias. By E. HECKEL and F. SCHLAGDENHAUFFEN (*Compt. rend.*, **109**, 382—385).—Araucarias differ from other coniferæ in that they secrete an oleo-gum-resin containing a large proportion of arabin. The secreting glands are at first normal and secrete oleo-resin, but at a certain time the cells bordering upon the glands elongate into papillæ, which converge to the centre of the glands, and completely obstruct the passage. From this time the neighbouring cells cease to secrete oleo-resin, become gelatinous, and are converted into liquid gum or arabin, which mixes with the oleo-resin previously secreted. At a particular time the glands are filled with a limpid liquid, which becomes white and opaque when exposed to air, and in which gum or oleo-resin predominates according to the species and time of year. *Araucaria Brasiliensis*, *A. Bidwilli*, *A. Cunninghami*, *A. excelsa*, and *A. Cooki* were examined.

The proportion of gum in the secretion from one and the same species varies from 86 to 59 per cent., and in different species, from 29 to 93 per cent. The secretion consists chiefly of gum, which usually contains a small quantity of glucose. In the case of *A. Bidwilli*, the portion of the secretion which is soluble in alcohol consists of a crystalline substance which dissolves in water and seems to be identical with *pinite*, the sugar found by Berthelot in *Pinus lambertiana*. All the oleo-resins and their essences are dextrogyrate in chloroform solution. The solutions in alcohol and in light petroleum contain no inorganic substances, but the portion soluble in water leaves an ash consisting mainly of calcium chloride, with some alkaline sulphates, calcium sulphate and carbonate, and small quantities of iron and manganese. C. H. B.

Protophyllin in Etiolated Plants. Py C. TIMIRIAZEFF (*Compt. rend.*, **109**, 414—416).—Protophyllin is obtained from chlorophyll free from xanthophyll (Abstr., 1886, 626); it shows an absorption-spectrum consisting of bands 2 and 4 of the chlorophyll spectrum. Oxidation is at once indicated by a reduction in the intensity of these bands, and the appearance of bands 1 and 3. Etiolated plants yield but very little protophyllin, and very deep layers of liquid must be used to observe the absorption spectrum. If very great care is taken to keep the plants completely in the dark, and to prevent oxidation of the protophyllin, its solution shows no trace of the chlorophyll band No. 1.

Protophyllin remains unaltered in an atmosphere of carbonic anhydride in the dark, but when exposed to light immediately becomes green. The author points out that he has never definitely asserted that the protophyllin reduces the carbonic anhydride. It is very difficult to ensure the absence of every trace of oxygen.

The decomposition of carbonic anhydride by the green parts of plants through the agency of chlorophyll must be attributed to the rays absorbed by the chlorophyll which is there from the beginning, and cannot fairly be ascribed to rays absorbed by protophyllin which is not present in the leaves and could only be formed by reduction of the chlorophyll. The strong absorption-band of protophyllin is in the orange, and these are also the rays which are most active in turning etiolated plants green (Reinke). The conversion of etiolated plants into green plants is due to the rays absorbed by the protophyllin, and the decomposition of carbonic anhydride is due to rays absorbed by the chlorophyll. C. H. B.

Atmospheric Nitrogen and Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, **109**, 210—213)—Hellriegel and Wilfarth have shown that microbes play an essential part in the absorption of atmospheric nitrogen by soils on which crops are growing. The author has therefore made experiments with eight soils taken from fields on which leguminosæ were growing, the assumption being that these soils would be charged with microbes, and hence any absorption of atmosphere nitrogen due to their influence would be well marked. The soils were dried by exposure to air, sifted, and introduced into large closed flasks, which were kept in a slightly warm place during winter. The atmosphere in the flask was renewed every week. The experiments lasted from August, 1888, to July, 1889, and the nitrogen was determined at the beginning and the end of the experiment. In all cases there was a slight loss of ammoniacal nitrogen, and a distinct increase in nitric nitrogen; but in almost all cases there was a slight loss of total nitrogen, and in no case was the gain of total nitrogen so much as 0·01 gram per kilo.

The results agree with the author's previous experiments, and he concludes that no soil which is not actually supporting vegetation can absorb nitrogen directly from the atmosphere. C. H. B.

Absorption of Nitrogen by Clay Soils. By BERTHELOT (*Compt. rend.*, **109**, 277—280).—Three years ago the author obtained results similar to those of Schloesing (preceding Abstract), and regarded them as proof that the absorption of nitrogen by soils was not simply a function of the soil but was conditioned by the presence of living microbes. He points out that Schloesing's experiments were made under conditions which are well known to be unfavourable to the absorption of nitrogen, and he also points out that many independent observers have confirmed his conclusion that soil which contains microbes and is supporting vegetable life has the power of absorbing nitrogen directly from the atmosphere. C. H. B.

The Relation of Atmospheric Nitrogen to Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, **109**, 345—349).—A reply in detail to the criticisms of Berthelot (preceding Abstract). C. H. B.

Influence of Electrification on the Absorption of Nitrogen by Vegetable Soils. By BERTHELOT (*Compt. rend.*, **109**, 281—287).—The soil, either alone or with living leguminosæ, was placed in an electric field, a constant difference of potential being maintained between the soil, which formed one surface of the field, and the plate of metal which formed the opposite surface of the field. The soil was exposed in both deep and shallow layers, sometimes with free circulation of air, sometimes in hermetically sealed globes, the duration of each experiment being about two months.

With thin layers of soil, freely exposed, there was no increase of nitrogen either under ordinary conditions or in an electric field with a difference of potential of 33 volts. In globes with a difference of potential of 33 volts, the nitrogen increased by 4·4 per cent. of its original amount, and with a difference of 132 volts, by 6·1 per cent.

Deep layers, in pots, of a soil nearly saturated with nitrogen gave an increase of 2 per cent. with free exposure to air without electrification, and 3·5 per cent. with free exposure in an electric field with a difference of potential of 33 volts. The same soil under similar conditions, but in globes, gained 2·7 and 4·0 per cent. respectively.

The same soil growing legumes with free exposure, gave an increase of 4·5 per cent. without electrification and 6·4 per cent. in the electric field. When enclosed in globes, the corresponding increases were 7·0 and 6·0 per cent. respectively. In another set of experiments, the gain with free exposure was 6·6 per cent. with electrification and 4·9 per cent. without; in globes, 7·1 per cent. in the electric field and 2 per cent. under ordinary conditions.

A soil comparatively poor in nitrogen and growing leguminosæ gave an increase of 22·4 per cent. with free exposure in the electric field, and 16·6 per cent. when not electrified.

These results show that the absorption of nitrogen is increased by electrification, and it is highly probable that this result is due to some peculiar influence of electricity on the soil and its vegetation.

C. H. B.

Absorption of Atmospheric Nitrogen. By Berthelot (*Compt. rend.*, **109**, 417—419).—The direct absorption of atmospheric nitrogen by soils under the influence of microbes and of vegetation may now be taken as definitely established. No such absorption occurs, however, with soils which have been sterilised or which are already saturated with nitrogen. C. H. B.

Evolution of Ammonia and Volatile Nitrogen Compounds from Vegetable Soils and from Plants. By Berthelot (*Compt. rend.*, **109**, 419—423).—Plants kept in moist closed spaces gradually perish, even in presence of suitable quantities of oxygen and carbonic anhydride. In the author's experiments on the absorption of nitrogen by plants in closed vessels, it was found necessary to change the atmosphere in the flasks frequently and completely, in order to ensure normal growth and development.

Plants growing in soil which was kept constantly moist were enclosed in glass vessels in such a manner that the water, which was evolved from the plant and the soil and condensed on the sides of the vessel, trickled down into a reservoir below, without coming in contact with the soil. From time to time this condensed water was drawn off and slightly acidified, and when a sufficient quantity of liquid had been collected the ammonia was determined by boiling with magnesia, and the nitrogen in the residual liquid was determined by means of soda-lime, after slightly acidifying and evaporating to dryness.

Vegetable soil supporting no plants gives off very small quantities of ammonia and volatile nitrogen compounds. In one experiment, with vegetable soil on which vetches were grown, all the evolved ammonia was re-absorbed by the plant, but the condensed water contained a very small quantity of volatile nitrogen compounds. With other leguminosæ, the condensed liquid contained ammonia and other nitrogen compounds, the quantities being of the same order of magnitude as with the soil supporting no vegetation. It is obvious, however, that the quantities of ammonia and volatile nitrogen compounds found in the water do not represent the total quantities evolved, since a considerable proportion will be re-absorbed by both the plants and the soil. The fact, however, that the volatile nitrogen compounds exhaled by animals are highly poisonous to the same animals (this vol., p. 629) gives considerable importance to the recognition of the exhalation of similar products from plants. C. H. B.

Nitrification of Ammonia. By T. SCHLOESING (*Compt. rend.*, **109**, 423—428).—The apparatus employed has been described in a previous paper. A definite quantity of an ammonium salt previously dissolved in water was carefully mixed with the soil, and the ammonia drawn from the flask while making it vacuous was absorbed in acid and estimated. The earth employed was rich in organic matter. Ammonium sulphate oxidises more rapidly than the chloride and carbonate; in all cases the quantity of free nitrogen in excess of that originally present in the air was within the error of experiment.

The increase in nitric nitrogen was practically equivalent to the loss of ammoniacal nitrogen, although it might have been expected that the nitrogenous matter in the soil would have undergone nitrification. It is known that in presence of nitrogenous organic matter the nitric ferment oxidises the carbon and hydrogen as well as the nitrogen, much more oxygen being utilised for the oxidation of the first two elements than for the nitrogen. It would seem, however, that in presence of ammonium salts the energy of the ferment is greatly increased, and it oxidises the ammonium salt, taking from the organic matter in the soil only the carbon which is necessary for its own growth and reproduction.

The rates of oxidation observed in the case of ammonium chloride, sulphate, and carbonate correspond respectively with the oxidation of 62, 168, and 75 kilos. per hectare per day. The conditions of the experiments are not strictly comparable with the conditions in an open field, but it is evident that under favourable conditions the nitrification of ammonium sulphate is much more rapid than is generally supposed. C. H. B.

Influence of Calcium Sulphate and of Clay on the Absorption of Nitrogen by Soils. By PÉCHARD (*Compt. rend.*, **109**, 445—447).—Almost pure sand was mixed with organic nitrogen in the form of oil-cake in the proportion of about 1 gram per litre, inoculated with the nitric ferment, and kept moist and free from vegetation for 18 months. The loss of nitrogen amounted to 70 per cent. of the original quantity, and was greater the coarser the sand; the ammoniacal and nitric nitrogen present in the sand at the end of the experiment were together less than 15 per cent. of the original quantity. Addition of 5 per cent. of calcium sulphate reduced the loss to 58 per cent., that which remained being mainly in the form of nitric nitrogen, with some ammonia. The effect was most marked with fine sand, and when the mixture was kept moist. The organic nitrogen is converted into ammonia before any traces of nitrous or nitric acids are formed. When nitrification does not proceed regularly, ammonia and ammonium carbonate are given off, and finally nitrogen is evolved in consequence of the interaction of ammonia and nitrous acid. The calcium sulphate partially converts the ammonia into ammonium sulphate, which is one of the most readily oxidised of its salts, but the calcium sulphate probably also plays a direct part in nitrification by reason of the ease with which it is reduced and re-oxidised, like sodium and potassium sulphates, which exert a similar although less marked effect. There is no reason to suppose that any atmospheric nitrogen was directly absorbed by the sand in the course of the experiments. Sodium chloride in the proportion of 1 gram per kilo. does not interfere with the action of the calcium sulphate, and, in fact, assists nitrification by keeping the mixture slightly moist.

The addition of 10 per cent. of pure clay reduces the loss of nitrogen, but an increase in nitric nitrogen is observed only with coarse sand; with fine sand the quantity is even slightly reduced. In both cases the quantity of ammonia is greater in consequence of the well-known absorptive power of clay for this substance.

With a mixture of 0·5 per cent. of calcium sulphate and 10 to 40 per cent. of clay, there is still less loss, especially in the case of fine sand, which even absorbs nitrogen directly from the atmosphere to the extent of 28·53 per cent. of the nitrogen originally present. In the case of coarse sand, the quantity of nitric nitrogen formed remains practically constant, but in other cases the quantity of nitric nitrogen, and also, though less rapidly, the quantity of ammonia, increases with the proportion of clay. In the absence of calcium sulphate the clay soon becomes saturated with ammonia, but the rapid nitrification which takes place in presence of the sulphate keeps the proportion of ammonia below the saturation point.

A soil composed of sand and clay, with some calcium phosphate, absorbed nitrogen directly from the atmosphere in amount equal to 26·8 per cent. of the organic nitrogen originally present.

Calcium sulphate in calcareous soils prevents the loss of ammonia in the form of ammonium carbonate; it is preferable to the oxide or to chalk as an addition to non-calcareous soils. Its effect is most marked in moist soils. The well-known beneficial influence of calcium sulphate, and of superphosphate which contains sulphate, on crops of leguminosæ is probably mainly due to the influence of the sulphate on nitrification. C. H. B.

Formation of Ammonia in Arable Soil. By A. Hébert (*Ann. Agron.*, 15, 355—369).—Moist earth sterilised by being heated for some time to 110° was found to have developed a certain quantity of ammonia; still more ammonia is formed at 130° and at 150°, so that the action of ferments is out of the question. The ammonia formed increases with the time of heating, but the greater part is formed the first two hours; for example, 100 grams of soil containing orig n

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ally 1·60 milligram of ammonia, contained after two hours at 150°, 15·17 milligrams; after four hours, 17·47 milligrams; after six hours, 18·63 milligrams; and after eight hours, 22·80 milligrams. The addition of ammonium sulphate to the soil before heating reduces the quantity of ammonia formed in a regular manner; thus, whilst in 100 grams of soil without addition, 10·04 milligrams of ammonia were formed during the heating, the addition of 10 milligrams of ammonium sulphate reduced the quantity formed to 9·24 milligrams, 20 milligrams of the salt to 8·92 milligrams, 50 milligrams of the salt to 8·23 milligrams, 100 milligrams of the salt to 3·47 milligrams, 150 milligrams of the salt to 2·19 milligrams, and 200 milligrams of the salt to −0·81 milligram. These facts seem to imply the formation of ammonia by purely chemical action, and a progressive dissociation, according to the quantity of ammonium salt present. The formation of ammonia still takes place with soil free from calcium carbonate or deprived of it by treatment with dilute acid and subsequent washing. With dry soil, however, little or no ammonia is produced, and the author believes that the source of the ammonia is the decomposition of complex amides contained in the soil by heating in contact with water.

J. M. H. M.

Sea Sludge and its Absorptive Power for Lime and Potash. By A. MÜLLER (*Landw. Versuchs-Stat.*, 36, 257—263).—The moors of Stensjöholm in Smaaland, South Sweden, consist partly of dried-up sea bottom. The present sea bottom is covered with an extremely fine sludge, which is almost black when wet and dark-grey when dry. 100 parts of the air-dry sludge contain:—7·88 parts of water; 20·72 parts of combustible matter (containing 0·737 part of nitrogen); 14·64 parts of ferric oxide, with some alumina; 0·34 part of phosphoric acid; 0·27 part of lime; 0·19 part of magnesia; and 0·19 part of potash. That portion of the sludge which is insoluble in hydrochloric acid contains (in 100 parts of original air-dried sludge):—soluble silicic acid, 33·23; alumina, with some ferric oxide, 4·11; lime, 0·72; magnesia, 0·23; alkalis, 0·77; and silica, 16·69 parts.

10·1 grams of air-dried sludge was digested several times with 0·14 per cent. lime-water until no more lime was taken up; it was found that the sludge had absorbed 2·95 per cent. of lime and 0·60 per cent. of alkali salt. It was not possible to determine how much of this was taken up by the silicic acid and how much by the organic matter of the sludge.

Similar experiments were made by digesting 10·1 grams of the sludge with 50 grams of a solution of 0·3615 gram of potassium carbonate for 14 days: the sludge absorbed 1·47 per cent. of potash, corresponding with 2·33 per cent. of potassium chloride or about 12 per cent. of kainite.

It is probable that the sludge would also absorb large quantities of phosphoric acid from superphosphates.

Silicic acid seems to form the best means for retaining plant food in the soil until required by plants, and it is suggested that the large amounts of silica found in, for instance, gramineous plants (which can be got to grow normally in solutions free from silica) acts in a similar manner within the plants themselves when these are so "insoluble" phosphate to pass into solution and become included in the water-soluble phosphates. The author cites a case in which neglect to use sufficient water gives rise to an error of this sort amounting to 3½ per cent. of soluble phosphoric acid. D. A. L.

Method of Rapid Evaporation for the Estimation of Silicon in Pig-iron. By C. JONES (*Chem. News*, **60**, 79—80).—The platinum dish containing the iron and nitro-sulphuric acid (Drown's method) is placed between two burners: one in the ordinary position beneath, the other inverted over the dish so that the flame shall play on the surface of the liquid; by this means evaporation is accelerated, whilst the current of heat and air on the surface prevents violent ebullition. The upper burner should be a blast-lamp; the lower one may be an ordinary Bunsen or a blast-lamp. D. A. L.

Volumetric Estimation of Mercury, Silver, and Thallium. By A. CARNOT (*Compt. rend.*, **109**, 177—179).—The method is based on the insolubility of mercuric and silver iodides in nitric acid when no alkaline iodide is present. 100 to 150 c.c. of the solution is mixed with 10 c.c. of nitric acid containing nitrous acid, some starch paste is added, and then a decinormal solution of potassium iodide gradually with continual agitation until a permanent blue coloration remains. The blue colour disappears very slowly towards the end of the reaction. It is better to make an approximate estimation, and then add nearly the whole of the potassium iodide at once, and finish the titration in the usual way. Free hydrochloric acid must not be present, nor any considerable quantity of the alkaline chlorides.

In the case of silver, it is better to add nearly the whole of the potassium iodide at once, agitate, decant off the clear liquid, and wash the precipitate by decantation. The liquid is now mixed with acid containing nitrous acid, and starch is added; if no blue coloration appears, it is titrated with potassium iodide; if, on the other hand, the liquid becomes blue, it is titrated with centinormal silver nitrate, the disappearance of the blue colour marking the end of the reaction. No hypoiodite is formed as in Pisani's method.

Thallium iodide being more soluble, the results are less accurate in this case. The dark colour of palladium iodide makes it impossible to use this method for the estimation of palladium. C. H. B.

Analysis of Glass. By D. LINDO (*Chem. News*, **60**, 14—15, 33, 41—42).—The pulverised glass is fused in a platinum crucible with a mixture consisting of 13 parts of potassium carbonate and 10 parts of sodium carbonate; the fused mass is dissolved in water, decomposed with hydrochloric acid, heated for some time, evaporated to dryness in a platinum dish, pulverised, again heated, moistened with hydrochloric acid and a little water, then after some time treated with water, heated, filtered, and washed. The washings are concentrated and mixed with the filtrate. The silica and filter ash are fused with the fusion mixture, dissolved as before, the solution diluted (this is important in order to obtain the silica in a vitreous state, when it is readily washed), decomposed, and the silica collected on a Gooch filter, washed, dried, &c. The filtrate and concentrated washings are mixed with those already obtained, and the combined solutions treated for the estimation of the dissolved silica, &c. Part of this solution is concentrated and treated with ammonia until a permanent precipitate is obtained, which is then dissolved by adding the remaining portion of the acid solution, hydrogen sulphide is passed through for 15 minutes, and after being two or three days in a closed flask, the whole is filtered. The filtrate is concentrated, any turbidity being removed by a few drops of nitric acid, and, while hot, is carefully precipitated by very slight excess of ammonia, then in a short time filtered, &c. The filtrate and concentrated washings, mixed with ammonia and ammonium sulphide to precipitate any manganese, are set aside for the estimation of calcium, magnesium, and the last traces of silica. In the ammonia precipitate, the silica, ferric oxide, alumina, and phosphoric acid are estimated by any of the four schemes described, which vary to suit circumstances: traces of phosphoric acid, however, and also the traces of calcium adhering to the ammonia precipitate may be disregarded. To obtain the last traces of silica from the above ammoniacal solution, an aliquot part is acidified with hydrochloric acid, filtered, mixed with 10 c.c. of ferric chloride of known strength, and precipitated hot with ammonia; the silica comes down with the ferric hydroxide. It is not necessary to remove the lime when it is present in moderate quantities. Lime and magnesia are estimated in the usual way. The results of the analysis of numerous samples of glass are appended to the original paper. D. A. L.

Spectro-colorimetric Estimation of Iron and Thiocyanates. By G. Krüss and H. Moraht (*Ber.*, 22, 2054—2060).—Experiments which were made with the object of estimating small quantities of ferric salts in presence of beryllium oxide by the converse of Vierordt's method (*Die Anwendung des Spectralapparates, Tübingen*, 1873, 146) for the estimation of thiocyanates gave results which caused the authors to redetermine the absorption constants of ferric thiocyanate. The values obtained differed materially from those given by Vierordt, as the reaction between ferric salts and thiocyanates does not take place in accordance with the equation $FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$, as is usually assumed.

The statement of Vierordt, that the absorption of the spectrum colours reaches a maximum when the ferric salt and the thiocyanate are in the molecular proportion of 1 : 3, is also incorrect.

The authors made a series of observations on the spectra of mixtures obtained by adding various quantities of a solution of potassium thiocyanate (1 c.c. = 0·01564 gram KCNS) to a solution of 1 c.c. of ferric chloride (1 c.c. = 0·00301 gram Fe) and sufficient water to dilute the mixture to 20 c.c. The strength of the two solutions employed is such that when 1 c.c. of the iron solution is mixed with [illegible] c.c. of the potassium thiocyanate 3 mols. of the latter are present to [illegible] the former. The results are given in tabular form. The extinction coefficients were found to increase gradually, and reach a maximum when 1 mol. of ferric chloride has been treated with exactly 12 mols. of potassium thiocyanate.

Similar observations were made employing a solution of ammonium thiocyanate instead of the potassium salt, and in another series of observations iron ammonia alum was substituted for the ferric chloride. The experiments showed that also under these conditions exactly 12 mols. of the thiocyanate must be added for every 1 mol. of the iron salt before the formation of the blood-red compound is complete. From these results it may be assumed that the coloured compound is not ferric thiocyanate, but a double salt of iron and potassium thiocyanate (compare p. 1129).

The absorption ratios calculated from the data obtained in the above experiments were made use of in attempts to estimate iron spectro-colorimetrically. Although the results obtained were probably more correct than those calculated by means of Vierordt's constants, the determinations cannot be relied on, as the double salt is very easily decomposed by water, acids, and salts. The measure of the decomposition is shown by the decrease in the extinction coefficients which occurs when a solution of the double salt is treated with various quantities of water, hydrochloric acid, and ammonium chloride respectively, and the results of observations in this direction are given in tables. The most remarkable phenomenon is the decomposition produced by water; when a solution of the double salt is diluted, some of the original iron salt is reproduced, so that the extinction coefficients are not proportional to the concentration of the solution, and consequently neither iron nor thiocyanates can be estimated by Vierordt's method. F. S. K.

Reduction of Ferric Sulphate in Volumetric Analysis. By C. Jones (*Chem. News*, **60**, 93—96).—The author recommends the reduction of ferric sulphate solution previous to titration with permanganate, by filtering through powdered zinc. An apparatus is described in which a tube filled with powdered zinc is connected with a flask. The ferric solution is allowed to run from a reservoir through an intermediate tube into this tube, while strong suction is applied to the flask below to overcome the interference produced by the hydrogen evolved. A filtering arrangement prevents any zinc or insoluble impurities from passing into the flask. D. A. L.

Elementary Analysis. By F. Blau (*Monatsh.*, **10**, 357—371).—A combustion-tube 114 cm. in length is placed in a 85 cm. Glaser's furnace, and is so arranged that it protrudes 10 cm. behind and 19 cm. in front of the furnace. To the tube are fitted the absorption-tubes containing calcium chloride and soda-lime, the latter being connected with a small Marriot's flask to serve as an aspirator, and with a small tube containing sulphuric acid to act as a pressure gauge. The combustion-tube contains, to the length of 60 cm., small rolls of fine copper gauze; this is first oxidised by heating in a current of oxygen, then reduced with hydrogen or alcohol vapour, and again oxidised, whereby an effective surface is obtained. If the compounds to be burnt contain halogens, the last roll of copper gauze is replaced by one of silver. The anterior portion of the tube, which stands out 19 cm. from the furnace, is filled to the extent of 10 cm. with granular lead peroxide, in order that sulphur dioxide and oxides of nitrogen may be absorbed. The posterior end of the combustion-tube is closed by a caoutchouc stopper, through which passes a T-piece of glass tubing along the horizontal portion of which passes a long glass rod, so as to just allow a stream of oxygen or air to find its way into the combustion-tube from the vertical arm of the T-piece. The glass rod is connected at its posterior end with the horizontal portion of the glass T-piece by means of a piece of sound caoutchouc tubing, which slides over both, so that the rod can be readily moved in and out of the combustion-tube without any leakage occurring, and is furnished with a platinum rake fused to its anterior end. By means of this contrivance it is possible to move the platinum boat, which is provided with an arm into which the rake can be easily twisted and untwisted, to and from the hotter parts of the combustion-tube, whereby the rate of combustion of the substance to be analysed may be arranged, with the help of the pressure gauge, to a nicety, and the time taken for the operation reduced to a minimum.

Appended are numbers obtained in the ultimate analysis by this method of sugar, colchicine, naphthalene, nitrobenzyl sulphide, and several other substances, showing the great saving of time which results. Even the most refractory substances may be burnt in 50 minutes, those burning more readily taking only from 20 to 30 minutes. G. T. M.

Simultaneous Estimation of Saccharose and Raffinose. By L. Lindet (*Compt. rend.*, **109**, 115—117).—When raffinose is estimated by Clerget's inversion method, the rotatory power of the raffinose is reduced by an increase of temperature, an increase in the proportion of acid, or by longer heating. In order to obtain constant results, the author proceeds in the following manner:—A 10 to 20 per cent. solution of sugar is heated at 100° on a water-bath, mixed with 20 per cent. of powdered zinc, and 20 per cent. of hydrochloric acid previously diluted with an equal volume of water is gradually added. The acid inverts the sugar, but is immediately afterwards neutralised by the zinc, and after all the sugar has been inverted the acid attacks the zinc in preference to attacking the invert sugar. The rotatory power is not affected even by the addition of as much as 40 per cent. of acid so long as the zinc remains in excess. Zinc oxide or carbonate acts in the same way as the metal, but neutralise the acid somewhat too rapidly. The evolution of hydrogen prevents the formation of coloured products. The rotatory power of the inverted sugars is the same whether the addition of the acid occupies 10 minutes or 40 minutes.

According to the author's measurements, the rotatory power of invert raffinose at 20° is +53°, and that of invert saccharose −20·1°.

In order to estimate saccharose or raffinose in a sugar solution, the rotatory power of the liquid is determined before and after inversion, and the relative proportions of the two sugars are obtained from the following equations, in which p and p' are the weights of saccharose and raffinose respectively, ρ and ρ' the rotatory powers before and after inversion, α and α' the rotatory powers of saccharose (+67·3°)

and raffinose (+103·6°) respectively, and β and β' the rotatory powers of invert saccharose (−20·1°) and invert raffinose (+53°).

$$p + p' = \rho \frac{\mathrm{V}}{\left(\frac{p}{p+p'}\alpha + \frac{p}{p+p'}\alpha'\right)l}$$

$$p + p' = \rho \frac{\mathrm{V}}{\left(\frac{p}{p+p'}\beta + \frac{p}{p+p'}\beta'\right)l},$$

from which $$p = p'\frac{\rho\beta' + \rho'\alpha'}{\rho\beta - \rho'\alpha}.$$

The results obtained with definite mixtures of raffinose and saccharose were very satisfactory. C. H. B.

Estimation of Formaldehyde by Titrating with Ammonia. By W. Eschweiler (*Ber.*, **22**, 1929—1930).—When methyl orange, congo-red, tropæoline, or cochineal is employed as indicator in titrating formaldehyde with ammonia, the basicity of the hexamethyleneamine which is produced must be taken into account (compare Lösekann, this vol., p. 1036), but when litmus or phenolphthaleïn is used the presence of hexamethylenediamine has no effect on the results.

Formaldehyde is only slowly acted on by dilute (about 1 per cent.) ammonia, and the mixture must be kept for one or two days, or heated at 100° for a short time to complete the reaction.

F. S. K.

Estimation of Uric Acid in Urine. By E. Salkowski (*Zeit. physiol. Chem.*, **14**, 31—51).—This article is very largely polemical. The author first shows how in his earliest papers on the subject, the possibility of estimating uric acid as a silver compound was mooted by him, and how this method was rejected, as there was found to be no constancy in the relation of silver to the uric acid in the compound formed. He then points out the inaccuracies of methods based by Haycraft, Hermann, and others on this fallacious foundation, and finally quotes experiments which confirm him in his original statement that the method is a bad one, the error of analysis averaging from 3 to 60 per cent. W. D. H.

Volumetric Estimation of Fat in Milk. By G. E. Patrick (*Chem. News*, **60**, 5).—The author employs for this purpose a calibrated tube about 30 cm. long, and about 17 mm. in diameter except for about 7 or 8 cm. near the middle, where it is narrowed to 5 mm., and is graduated in divisions of 0·025 c.c. each; the lower portion has a capacity of 21—22 c.c., and is pierced by a lateral perforation, which can be closed by an indiarubber band. 10·8 c.c. of milk is placed in this tube, and then, in two lots, 15 c.c. of a mixture of strong acetic acid, strong sulphuric acid, and concentrated hydrochloric acid, in proportions of about 9, 5, and 2 by volume; the first portion of this mixture being well mixed with the milk. The charged tube is boiled briskly for 10 minutes, and then gently for the same time or until the fat collects as a clear layer on the top. The tube is now cooled to 60°, and by letting some of the liquid flow from the lateral perforation the fat is lowered into the narrow part of the tube and its volume read off. If, however, great accuracy is required, the fat adhering to the sides is washed down with ether, the tube heated to expel the ether, again cooled to 60°, and the volume read. At 60° with 10·8 c.c. of milk, 1 division on the tube represents 0·2 per cent. of fat. The acid mixture is intended to dissolve all but the fat, and is made by mixing the acetic and sulphuric acids, the hydrochloric acid being added to this mixture when cool. The above proportions may be varied, and so may be the quantity of the mixture added to the milk, without affecting the result. Larger proportions of hydrochloric acid, however, render the milk solution turbid, whilst increasing the amount of acetic acid retards the solution somewhat, but gives a clear and lighter coloured liquid. D. A. L.

Estimation of Fat in Linseed Cake. By E. WRAMPELMEYER (*Landw. Versuchs-Stat.*, **36**, 287—295).—The best solvent for extracting the fat is ether; this need not be perfectly dry; treatment of the ether with calcium chloride dries it sufficiently. The air-dried cake (3 grams) is weighed, dried for an hour at 100° in a stream of coal-gas or hydrogen, and extracted for three hours in a syphon apparatus, the heating of which is to be so arranged that the syphon works every minute or minute and a half. The ether is then distilled off, and the residue heated at 95—98° for one hour in a L. Meyer's drying oven. It is shown that if the residue is thus quickly dried the results differ only slightly from those obtained when the substance is dried in an atmosphere free from oxygen.

N. H. M.

Reactions of Oils with Silver Nitrate. By R. BRULLÉ (*Compt. rend.*, **109**, 118—119).—10 c.c. of the oil is mixed with 0·5 c.c. of fuming nitric acid in a porcelain dish, and heated with vigorous agitation until a paste is formed, which will have a colour depending on the nature of the oil. 5 c.c. of a 2·5 per cent. solution of silver nitrate in alcohol of 90° is now added, and the mixture is heated to about 115°, when the silver nitrate suddenly decomposes with separation of silver. Heating is continued until the first reflections disappear, and the colour of the thin film of liquid against the sides of the dish, and the metallic lustre on the surface, are then observed. If the oils are previously saponified, and are then treated in the same way, different colorations are obtained.

Oil.	Natural oil.		Saponified oil.	
	Oily layer.	Surface reflection.	Oily layer.	Surface reflection.
Olive	Olive green	Green	Mars orange	Cyprus green.
Cotton-seed	Green	Ash green	Raw sienna	Cobalt violet.
Sesamé	Chrome green	Pale Sèvres blue	Golden yellow	Cobalt violet.
Earth nut	Greenish yellow	Emerald green	Persian lake	Pale violet.
Poppy	Olive green	Pale bluish green	Golden ochre	Blue.
Camelina	Persian lake	Pale blue	Deep chrome	Blue.
Linseed	Dragon's blood	Emerald green	Black	Green.
Colza	Persian lake	Cyprus green	Burnt carmine	Ultramarine.

The names given to the colours are those commonly employed by water-colour painters. C. H. B.

Error in the Detection of Albumin. By C. PATEIN (*Compt. rend.*, **109**, 268—270).—The author has found in urine and in tumours an albumin which behaves like other albumins, and is coagulated by potassium ferrocyanide or magnesium sulphate in presence of acetic acid, also by heat and by nitric acid, but if after coagulation by nitric acid, a few drops of acetic acid are added to the liquid, the albumin completely and immediately redissolves. It follows that in detecting and estimating albumin, the use of acetic acid may introduce a considerable error. The proper method of procedure is to precipitate the "hydropisin" (? plasmin) in one portion by means of magnesium sulphate; to precipitate the "serein" (? serum albumin) and hydropisin together in a second portion by means of heat and a few drops of acetic acid, and to acidify the filtrate from this precipitate with nitric acid and again heat, when the peculiar albumin in question is thrown down. C. H. B.

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ERRATA.

VOL. XLVIII. (1885.)

Page	Line		
556	5 from top, *et seq.*		*for* "pyrazene" *read* "pyrazole."
810	26 „ „ „		
1247	15 „ bottom, „		

VOL. L. (1886.)

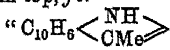
1103	col. ii, line 17 from bottom, *for* "1040"	*read* "1014."

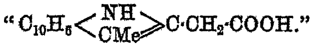
VOL. LII. (1887.)

436	20	from bottom, *for* "*Ann. Chim. Phys.*"	*read* "*Ann. Phys. Chem.*"
465	14	„ top, „ "Gutnecht"	*read* "Gutknecht."
465	21	„ bottom, „ "benzoimide"	„ "benzoïmide."
603	10	„ top, „ "phenylmethylpyrazine"	*read* "phenylmethylpyrazole."
678	16	„ bottom, „ "phenylhydrazinobenzalacetone"	*read* "phenylhydrazinebenzalacetone."
1151	5	from top, col. ii, *insert*	"AMPHLETT, E. G., and H. E. ARMSTRONG. Isomeric change in the naphthalene series, No. 2. β-Ethoxynaphthalenesulphonic acids, Proc., 144."
1152	30	„ „ „ i, „	"ARMSTRONG, H. E. Isomeric change in the naphthalene series, No. 1, Proc., 143."
1152	33	„ „ „ i, „	"ARMSTRONG, H. E., and S. WILLIAMSON. Isomeric change in the naphthalene series, No. 4. α-Haloidnaphthalenesulphonic acids, Proc., 145."
1152	37	„ „ „ i, „	"ARMSTRONG, H. E., and W. P. WYNNE. Isomeric change in the naphthalene series, No. 3. β-Chloronaphthalenesulphonic acids, Proc., 145."
1152	40	„ „ „ i, „	"——— the sulphonation of naphthalene, Proc., 146."
„	„	„ „ „ i, „	"ARMSTRONG, H. E. See also AMPHLETT."
1187	10	„ bottom „ ii, „	"STOKES, A. W. An apparatus for the comparison of colour tints, Proc., 135."

VOL. LIV. (1888.)

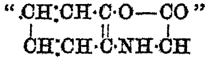
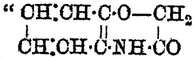
285	1	from top, *for* "$C_{10}H_6{<}{}^{NH}_{CMe}{>}C\cdot COOH$"	*read*	"$C_{10}H_6{<}{}^{NH}_{CMe}{>}C\cdot CH_2\cdot COOH$."
960	2	„ „ „ "The bases after separation from the hydrochlorides are,"	*read*	"except that the amyl alcohol layer is acidified with hydrochloric acid, the liquid evaporated to a small bulk, and the hydrochlorides which separate, after washing with ether, are converted into the free bases; these are then."
961	10	„ „ „ "to which the amido-group is united"	„	"to which the amido-group is not united."
1088		top, *for* "propiophene"	*read*	"propiophenone."
1354	19	from top, col. i, *for* "W. O. WYNNE,"	*read*	"W. P. WYNNE."
1398	34	„ „ „ i, *insert* "WYNNE, W. P. See ARMSTRONG."		


$C_{10}H_6{<}{}^{NH}_{CMe}{>}C\cdot COOH$


$C_{10}H_6{<}{}^{NH}_{CMe}{>}C\cdot CH_2\cdot COOH$

ERRATA.

Vol. LVI. (1889.)

Page	Line	
59	16	from top. *for* "Methyldihydropyrroline" *read* "Methyldihydroparvoline."
59	20	,, ,, "$C_{17}H_{17}N,HAuCl_4$" ,, "$C_{10}H_{17}N,HAuCl_4$."
67	17 & 15	from bottom, *for* "turnesole" *read* "litmus."
135	27	,, top, ,, "P. Jacobsen" *read* "P. Jacobson."
178	22	,, ,, ,, "Hoffmann" ,, "Hofmann."
226		top, *for* "A. Muntz" *read* "A. Müntz."
230		,, "platino-" *read* "platini-."
249	5 & 12	from bottom, *for* "tetrole," *read* "tetrene."
281	26	from top, *for* "amorphous" *read* "anhydrous."
323	5	,, ,, *et seq.* The process described here was stated in Kremel's original paper (*Pharm. Post*, 21, 534) to be quoted from a paper by W. R. Dunstan and T. W. Short (*Pharm. J. Trans.* [3], 13, 666).
331	10	,, bottom, *for* "C. Shall" *read* "O. Schall."
385	4	,, ,, ,, "30 per cent." *read* "3 per cent."
366	15	,, ,, ,, "butyric" ,, "butyl."
394	16	,, top, ,, "permanganate" *read* "ferricyanide."
411	18	,, ,, ,, "Phenylquinic acid" *read* "Phenylquininic acid."
429	27	,, bottom, ,, "24" ,, "25."
443	bottom	,, "95" ,, "59."
444	23	from top, after "ammonia" *insert* "reacidified with sulphuric acid, treated with 50 c.c. of a solution of sulphurous anhydride, diluted to 900 c.c. with boiling water."
459	4	,, bottom, *for* "formation" *read* "combustion."
490	2	,, ,, *et seq. for* "kepitic acid" *read* "ketipic acid."
491	4	,, top, *et seq.* ,, "kepitate" ,, "ketipate."
566	5	,, ,, *for* "Tamman" *read* "Tammann."
592	8	,, ,, *et seq. for* "β-ketonic ethers" *read* "ethereal salts of β-ketonic acids."
626	13	,, ,, } *for* "quinic acid" *read* "quininic acid."
,,	14	,, bottom }
834	8	,, top, *for* "Chloride" *read* "Chlorides."
868	9	from bottom, *for* "nitropyrocatechol" *read* "nitrocatechol."
888	21, 29	,, top } ,, "alicylic" ,, "alicyclic."
889	5, 6	,, bottom }
890	15	,, ,, }
891	8, 22, 29	,, top }
901	13	,, ,, ,, "coniceïns" ,, "coniceïnes."
911	6	,, ,, ,, "anti-albuminoïd" ,, "anti-albumid."
912	6	,, bottom, ,, "just" ,, "first."
923	28	,, top, ,, "A. Muntz" *read* "A. Müntz."
944	2	,, ,, ,, "have" *read* "has."
990	12	,, bottom, ,, " $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}O—CO}\\ \mathrm{CH{:}CH{\cdot}C{\cdot}NH{\cdot}CH}\end{array}$" *read* " $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}O—CH_2}\\ \mathrm{CH{:}CH{\cdot}C{\cdot}NH{\cdot}CO}\end{array}$".
999	3	,, ,, ,, "S. Hooker" *read* "S. C. Hooker."
1033	12	,, ,, ,, "F. Moore" ,, "T. Moore."
1033	24	,, ,, ,, "E. P. Dewey" *read* "F. P. Dewey."
1036	6	,, ,, ,, "Losekann" *read* "Lösekann."
1091	13	,, ,, ,, "Sortegné" *read* "Sostegni."
1152	7	,, ,, ,, "Tetrabenzoylerythrite" *read* "Tetrabenzoylerythrol."

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